ARCHIVES OF ENVIRONMENTAL PROTECTION
vol. 34 no.3 pp. 169 - 181 2008
PL ISSN 0324-8461

PATHWAYS OF POLYCHLORINATED DIBENZOTHIOPHENES (PCDTs) IN THE ENVIRONMENT

JACEK CZERWIŃSKI

Laboratory of Environmental Analyses, Faculty of Environmental Engineering
Lublin University of Technology, 40B Nadbystrzycka str., 20-618 Lublin, Poland
E-mail: j.czerwinski@wis.pol.lublin.pl, tel. +48 081 5384414

Abstract: Pathways of PCDTs and PCTAs in the environment are discussed. Data on levels of these compounds in various part of the environment and their possible sources are presented. Finally, the data on biological effects of PCDTs and PCTAs based on some preliminary toxicological investigations are given.

Keywords: Dioxin like compounds, dioxins sulphur analogues, chlorinated dibenzothiophenes and thianthrenes

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) are well known contaminants ubiquitous in the present environment. Due to their lipophilicity and resistance to bacterial metabolism or chemical degradation these compounds have the potential to accumulate in the food chain and cause toxic effects. Polychlorinated dibenzothiophenes (PCDTs) constituting the sulfur analogues of polychlorinated dibenzofurans (PCDFs) and polychlorinated thianthrenes (PCTAs) are sulfur analogues of polychlorinated dibenzo-*p*-dioxins (PCDDs). Due to their structural similarity with dioxins they constitute a group of compounds environmentally and toxicologically interesting.

Figure 1 present structures of sulfur analogues of polychlorinated dibenzodioxins, furans and diphenyl thioethers.

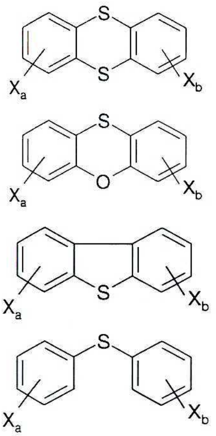


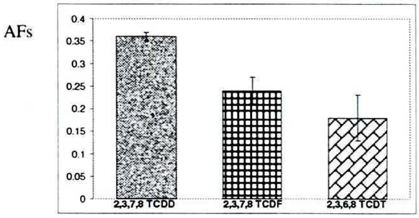
Fig. 1. Structures of polychlorinated thianthrenes, phenoxatyines, dibenzothiophenes and diphenyl thioethers.

TOXICOLOGY OF SULPHUR ANALOGUES OF DIOXINS

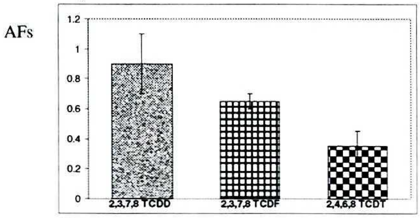
The sulphur analogous of dioxins and furans are compounds which are related to the dioxins and furans. Therefore, their mechanism of effect corresponds to that of dioxins and furans. They belong to the compounds which possess a potential of negatively affecting the Ah receptor-mediated mechanism; therefore, in the literature, there is discussion of a toxicity which is typical for dioxins. *[Kopponen at al., 1994, Giesy et al., 1997].*

The current state of art on toxicological data of these compounds suggests that PCDTs have similar to PCDFs TEF factors, while PCTAs TEF factors are significantly lower (three orders of magnitude). 2,3,7,8-subsituted PCDTs have been found as an arylohydrocarbon hydroxylase and EROD inductors.

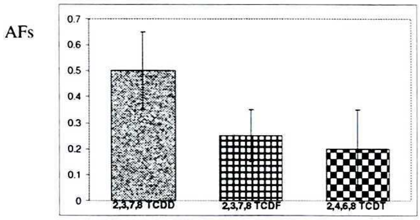
Three important reports related to a high, dioxin-like toxicity of sulphur-analogues of polychlorinated dibenzofurans has appeared in the literature in recent years *[Hosomi et al 2005, Nakai et al 2004, 2006].* In prior works *Kopponen et al. [1994]* analysed the influence of three organosulphur compounds: 2,3,7,8-TCTA (tetra-chlorothianthrene), 2,3,7,8-TCDT (tetrachlorodibenzothiophene and 3,3',4,4'PCDPS (tetrachlorodiphenyl-thioether) – sulphur analogue of tetrachlorodiphenylether, on the induction of CYP1A1 gene expression, which was measured as an activity of aryl hydrocarbon hydroxylase (AHH) and ethoxyresorufin-*O*-deethylase (EROD) in liver cells of Hepa-1 mice. Significant differences between 2,3,7,8-TCDT and the analysed sulphur analogs in EROD and AHH activity were observed. They found EC (50) values as follows: 2,3,7,8-TCTA - 700 [pM]; 2,3,7,8-TCDT – 7500 [pM] and they do not observed the response for 3,3',4,4'-TCDPS. Calculated **R**esponse **E**quivalency **P**otencies (REP) for these compounds were respectively: 0.011; 0.001 and 0. Moreover, the value of the REP factor (0.00425) was estimated by Giesy for a synthetic mixture of PCDT congeners in the H-4IIE rat liver cells *[Kopponen et al.1997].*



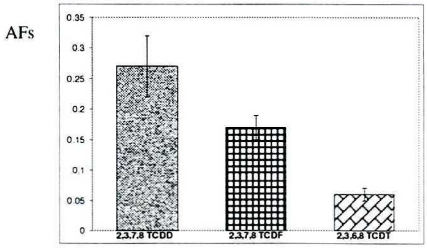
Polycheates



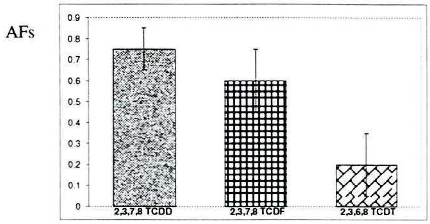
Clams



Sandworms



Lobster muscules



Lobster hepatopancreas

Fig. 2. Accumulation factors of TCDD, TCDF and TCDT by different marine biota *[Pruell et al, 1993, 2000]*

Analogous studies of Ah immunoenzymatic activity were also run for a number of dioxin-like congeners of polychlorinated dibenzothiophenes by a group of researchers from Tokyo University *[Hosomi et al. 2005, Nakai et al. 2004, 2006]*. The above research was carried out using a high-tech Ah-immunoassay® test (Paracelsian USA). Nakai and Hosomi found EC (50) values for 2,3,7,8-TCDT – 111 [pM], 1,2,3,7,8-PeCDT (pentachlorodibenzothiophene) – 117 [pM]; 1,2,3,7,8,9-HxCDT (hexachlorodibenzothiophene) – 44 [pM]; 1,2,3,4,7,8,9-HpCDT (heptachlorodibenzothiophene) – 50 [pM], and found no response for octachlorodibenzothiophene. Calculated REP factors were as follows: 2,3,7,8-TCDT – 0.1; 1,2,3,7,8-PeCDT – 0.1; 1,2,3,7,8,9-HxCDT – 0.04; 1,2,3,4,7,8,9-HpCDT – 0.05. Similar e-TEF factors were obtained by Kobayashi *[1999]*.

These investigations, showing much higher values of the dioxin-like toxicity of polychlorinated dibenzotiophenes have caused growing interest in their presence in different compartments of the environment *[Sinkkonen et al. 1997, 2001, 2003]*.

Calculations of Accumulation Factors (AFs) [(organism/lipid)/(sediment/TOC)] on real samples were made by Pruell et al. *[1993, 2000]* in the Passaic River, New Jersey. In this study three species accumulated: 2,3,7,8-tetrachlorodibenzo-p-dioxin, 2,3,7,8-Tetrachlorodibenzo-furan, polychlorinated biphenyls and the sulphur analogue 2,4,6,8-tetrachlorodibenzothiophene. Results were used o compare among species and compounds. These comparison showed that steady-state AFs values were obtained fastest for clams –*Macoma nasuta* (10 days), for shrimps, *Palemonetes pugio* - 28 days and after 70-120 days steady-state AFs values were not obtained for sandworms *Nereis virens*. Generally higher accumulation factors (AFs) were obtained for crabs, homars (muscles and hepatopancreas) and venus clams while they were lower for sandworms. However, the AFs for 2,4,6,8-TCDT were significantly higher for crabs than for sandworms and venus clams. This may be due to different metabolism or to a species dependent composition of adipose tissue which leads to a different accumulation in the tissue *[1993, 2000]*. Calculation of chemical stability of PCDTs were made by Chen et al. *[2007]*. These data present that PCDTs have similar stability to the PCDFs. Table 1 shows most stable and unstable congeners of polychlorinated dibenzothiophenes in comparison to the polychlorinated dibenzofurans.

Table 1. Most stable and unstable congeners of PCDTs and PCDFs *[Chen et al, 2007]*

	Most stable congeners		Most unstable congeners	
	Dibenzothiophenes	Dibenzofuranes	Dibenzothiophenes	Dibenzofuranes
Mono-	2-, 3-	2-, 3-	1-	4-
Di-	2,7- 3,7-	1,7-	1,9-	1,9-
Tri-	2,4,7-	1,3,7-	1,2,9-	1,2,9-
Tetra-	2,4,6,8-	1,3,6,8-	1,2,8,9-	1,2,8,9-
Penta-	1,3,4,6,8-	1,3,4,6,8-	1,2,3,4,9-	1,2,3,8,9-
Hexa-	1,3,4,6,7,8-	1,2,4,6,7,8-	1,2,3,4,8,9-	1,2,3,4,8,9-
Hepta-	1,2,3,4,6,7,8-	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-	1,2,3,4,7,8,9-

The oral intake of differently high doses of TCTA and, for comparison, of TCDD, led in Wistar rats at high TCTA doses to a significant reduction of the rate increase of body weight and of the weight of thymus and spleen and increased the microsomal CYP content in the liver as well as the EROD activity in male Wistar rats. The NOAEL was found to be for TCTA 1µg/(kg × 14 days) and for TCDD in female rats 0,001µg/(kg × day). This study shows that TCTA is less toxic to rats than TCDD *[Petersen et al. 1993]*. A subchronic study with NMRI mice in which doses were used which corresponded to the lethal TCDD doses in mice yielded no evidence of a weight loss or other obvious signs of toxicity *[Weber et al. 1998]*.

The kinetics of elimination and the toxicity of 2,3,7,8-tetrachlorothianthrene were studied with NMRI mice and with mice liver homogenate. The rate of metabolisation of TCTA in mice liver homogenate was comparable to that of PCDDs not substituted at the 2,3,7,8 positions, while TCDD and 2,3,7,8,-TCDF do not metabolise within such short time (4 hours) under comparable conditions. TCTA is rapidly removed from the liver and the entire body.

The studies performed with NMRI mice yielded a much lower half-life of 1 day for TCTA in male NMRI mice as compared to TCDD which had a half life of 8,5 to 24 days *[Weber et al. 1998]*.

FORMATION OF SULPHUR ANALOGUES OF DIOXINS

According to present knowledge the sulphur analogues of dioxins and furans always occur in conjunction with dioxins and furans. This allows an assumption of similar preconditions for the formation of these two groups of compounds. (In figures 3-6 possible formation pathway are presented). Therefore, it no surprise that the pathways of their thermal formation run in parallel. The comparison of the formation of PCDTs from PCBs in presence of elemental sulphur derived in the laboratory (see figure 6) with the familiar ring formation and conversion of 3,3',4,4'-tetrachlorobiphenyl to 2,3,7,8- tetrachlorodibenzofuran is shown in the following figures (figures 3,4,5: example of a ring forming reaction). PCDTs can be formed in chemical processes analogous to those that lead to the formation of PCDFs. Condensation of chlorothiophenols instead of chloro phenols could lead to the formation of PCDTs. Other possibilities are reactions of elemental sulfur in the presence of some metal catalysts or reactions of some reactive sulfur compounds with polychlorinated biphenyls (PCBs). The major known sources of PCDTs in environment are combustion and metallurgy. PCDTs are known to be formed in waste incineration *[Sinkkonen, 2003]*, incineration of PCB, and in metal recycling processes *[Aittola et al., 1996, Sinkkonen et al. 1997]*. Till now, PCDTs and also alkylated PCDTs are found, though in very low concentrations, in pulp mill effluents and sediments *[Cai et al. 1994, Sinkkonen et al. 2001]*. Other potential sources of PCDTs are automobile exhaust, wood combustion, oil/gas heating, chemical production of PCBs and trichlorobenzene sulfonates, and sewage sludge *[Huntley et al. 1994, 1998]*. One possible source is the ancient use of PCB/sulfur formulations to impart physical and chemical properties such as moisture resistance and flame resistance, adhesion properties, etc. of the products in the preparation of cloth, paper, and wood *[Sinkkonen et al. 2001]*. Rappe et al. have suggested that PCDTs in the environment could be used as indicators of production and manufacture of iron and steel and have proposed that 2,4,6,8-TeCDT could be a unique chemical marker from a former 2,4,5-T manufacturing facility *[Rappe 2004]*. However, sulfur-containing chemicals are not used in the synthesis of 2,4,5-T *[Huntley et al. 1998]*. Organochlorine compounds such as chlorobenzenes, chlorophenols, PCBs, PCDDs, and PCDFs are formed as unwanted byproducts in metal reclamation. PVC and other chlorine-containing compounds in the raw materials and chlorine-containing chemicals in the reclamation process are possible precursors as well as the so-called *de novo* synthesis *[Bechtler et al. 1998]*. Gas phase samples from an aluminum smelter and a car shredder and ash have been found to contain PCDTs *[Aittola et al. 1996]*. The ash was from different processes where the temperatures varied from 350 to 850°C. Raw materials in the aluminum smelter are floated aluminum, dried turnings, Al-sheets and Al-dross. NaCl/KCl is used in the flux. Temperature in the aluminum smelting is from 800 to 1200°C. The gases from the smelting process are cooled and cleaned by a baghouse filter. In the car shredder the cars are crushed and different materials are separated in a screening system. The highest temperatures during the shredding process are 600–700°C - the temperatures almost optimal for the PCDT formation.

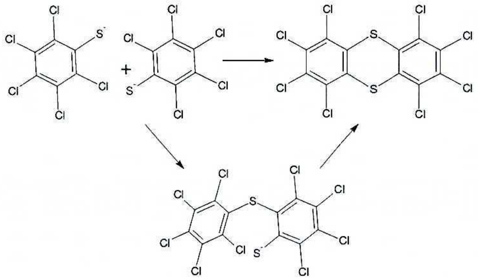


Fig. 3. Formation of octachlorothianthrene by dimerization of pentachlorothiophenate *[Benz et al. 1992]*

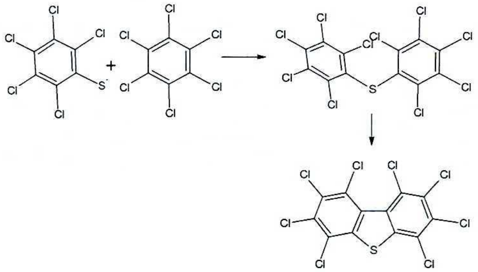


Fig. 4. Formation of octachlorodibenzothiophene by a cyclization of bis(pentachlorophenyl)thioether. *[Benz et al. 1992]*

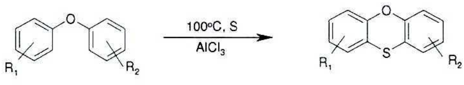


Fig. 5. Formation of phenoxatyine by Ackermann reaction.

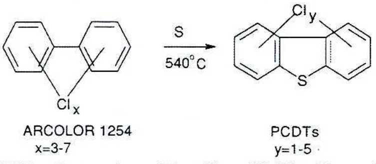


Fig. 6. Formation of PCDTs via reaction with sulfur of PCBs *[Buser 1992, Sinkkonen 1997]*

LEVELS OF PCDTS IN THE ENVIRONMENT

The concentrations of TriCDTs, TeCDTs, and PeCDTs in soil and sediment samples, gas samples from waste incineration and aluminum smelting, ash from an aluminum smelting plant, a car shredder, and from combustion of wood chips, peat and refuse derived fuel, different effluents from a pulp and paper mill, and crab, carp, and lobster tissue samples, are presented in Tables 2, 3 and 4.

Table 2. Levels of polychlorinated dibenzothiophenes in industrial samples and processes wastes

Type of sample	PCDT congeners						PCDD congeners	PCDF congeners	Reference
	Tri-	Tetra-	Penta-	Hexa-	Hepta-	Octa-			
Emissions ng/m^3 of chlorodibenzothiophenes (PCDTs) from Al-smelter and car schredder , Averages of the measurements in 1993 (N = 4)									
Al smelter before filter	256.9	186.2	55.3	n.a.	n.a.	n.a.	2378-TeCDD 656	2378-TeCDF 334	Aittola 1996
Al smelter before filter	33.7	12.6	2.68	n.a.	n.a.	n.a.			
Car schredder Before scruber	<0.05	<0.05	<0.05	n.a.	n.a.	n.a.	2378-TeCDD 219	2378-TeCDF 145	
Car schredder Before scruber	<0.05	<0.05	<0.05	n.a.	n.a.	n.a.			
Fly ash samples combusted solid fuel used in the combustions series									
100% of wood chips	430	40	n.a.	n.a.	n.a.	n.a.	80*		Sinkkonen 1995
85% of wood chips, 15% of RDF	560	<30	n.a.	n.a.	n.a.	n.a.	13440		
70% of wood chips, 30% of RDF	60	<30	n.a.	n.a.	n.a.	n.a.	12270		
55% of wood chips, 45% of RDF	40	<30	n.a.	n.a.	n.a.	n.a.	1910		
milled peat	60	<30	n.a.	n.a.	n.a.		600		
85% of peat, 15% of RDF	90	40	n.a.	n.a.	n.a.	n.a.	380		
85% of peat, 15% of RDF	50	<30	n.a.	n.a.	n.a.	n.a.	610		
70% of peat, 30% of RDF	40	<30	n.a.	n.a.	n.a.	n.a.	400		
Formation of polychlorinated sulfur-compounds in dependence of the sulfur content at 350°, 400° and 450°C [ng/g fly ash]									
350°C, 1% S	n.a.	38.4	30.5	14.2	3.0	0.0	2747	8151	Bechtler 1998
350°C, 2 % S	n.a.	166.9	218.8	157.7	22.1	0.3	8404	10869	
350°C, 3 % S	n.a.	217.0	278.5	281.3	77.9	6.0	7395	8325	
400°C, 0 % S	n.a.	61.0	50.5	11.8	9.5	0.2	638	4550	
400°C, 1% S	n.a.	57.3	43.4	18.8	4.3	0.2	2552	8755	
400°C, 2% S	n.a.	101.4	79.3	48.6	10.9	0.1	3883	6742	
400°C, 3% S	n.a.	233.0	292.0	314.5	100.9	8.2	5105	7491	
450°C, 1% S	n.a.	20.7	33.8	24.3	6.7	0.4	675	4078	
450°C, 2% S	n.a.	17.2	15.5	6.7	1.0	0.2	948	3567	
450°C, 3% S	n.a.	45.4	57.7	42.7	7.4	0.3	1217	3300	
Ashes from different combustion experiments In Standard boiler ng/kg									
Coal from Bogdanka mine	n.a.	27	36	25	6	n.d.			Czerwinski 2007
Beech wood	n.a.	13	6	12	n.d.	n.d.			
Waste paper	n.a.	45	79	13.2	23	n.d.			
willow	n.a.	89	75	24.5	34.6	n.d.			
Coke dust	n.a.	<1	<2	<2	<3	<5			
Fly ash	n.a.	<1	<2	<2	<3	<5			
Sludge	n.a.	37	42	25	11	<5			

*tetra CDD pg/g

Table 3. Levels of polychlorinated dibenzothiophenes in environmental samples (soil and bottom sediments)

Sampling site	**PCDT congeners**						**PCDD congeners**	**PCDF congeners**	**Reference**
	Tri-	**Tetra-**	**Penta-**	**Hexa-**	**Hepta-**	**Octa-**			
Bottom sediments from Passaic River (USA) ng/kg d.m.									
	n.a.	2,4,6,8-TeCDT 3680	n.a.	n.a.	n.a.	n.a.	2378-TeCDD 656	2378-TeCDF 334	Pruell 1993
	n.a.	2,4,6,8-TeCDT 1280	n.a.	n.a.	n.a.	n.a.	2378-TeCDD 219	2378-TeCDF 145	Pruell 2000
Surface sediments from Elbe River ng/kg d.m. (sum of congeners)									
Meissen km 83.2	845	<4	n.a.	n.a.	n.a.	<7			Claus 1998
Saale inflow km 252.0	1710	<4	n.a.	n.a.	n.a.	220			
Dessau km 261.4	2160	<4	n.a.	n.a.	n.a.	280			
Magdeburg km 319.4	1150	<4	n.a.	n.a.	n.a.	120			
Lostauer Bogen km 337.3	470	<4	n.a.	n.a.	n.a.	210			
Wittenberge km 454.9	1160	<4	n.a.	n.a.	n.a.	200			
Surface and deep sediments from Kimijoki River (Finland) ng/kg d.m. (sum of congeners)									
Lopotti km 10, 0-3 cm	n.a.	386.0	174.0	<5		<5	n.a.	n.a.	Sinkkonen 2001
Lopotti km 10, 3-6 cm	n.a.	102.0	30.0	<5		<5			
Koskenalus km 18, 0-3 cm	n.a.	76.0	20.0	<5			n.a.	n.a.	
Muhjärvi km 25, 6-9 cm	n.a.	<5	<5	<5			n.a.	n.a.	
Hirvivuolle km 32, 0-3 cm	n.a.	105.0	<5	<5			n.a.	n.a.	
Hirvivuolle km 32, 6-9 cm	n.a.	25.0	6.0	6.0					
Vastila km 36, 0-3 cm	n.a.	22.0	127.0	31.0			n.a.	n.a.	
Tammijärvi km 40, 0-3 cm	n.a.	63.0	<5	<5					
Tammijärvi km 40, 6-9 cm	n.a.	42.0	30.0	40.0					
Surface sediment 0.5 km from pulp mill	20	2	n.d.						Sinkkonen 1994
Sediment 0.5 km from pulp mill 9-12 cm	10	n.d.	n.d.						
Surface sediment 9 km from pulp mill	10	n.d.	n.d.						
Surface sediments Saginaw Bay [ng/kg w.m]									
	Σ PCDT 10-500								Giesy 1997
SOILS									
Soil sample*	Σ PCDT 67000ng/g								Petermann 1986
Sample A	n.a.	990	610				TeCDD 630 Σ PCDD 120430	TeCDF 12000 Σ PCDF 439000	Nakai 2004
Sample B	n.a.	1700	1700				TeCDD 3600 Σ PCDD 12700	TeCDF 24000 Σ PCDF 55100	

* from a waste pit where electrical PCB capacitors were incinerated, n.a. – not analysed, n.d. – not detected

Table 4. Polychlorinated dibenzothiophenes in biota samples

Sample/ sampling site	**PCDT congeners**				**PCDD/F congeners**	**Uwagi**	**Reference**
	Tri-	Tetra-	Penta-	Other congeners			
Crabs Elizabeth, Newark Bay	140 pg/g	2,4,6,8-TCDT 8300 pg/g Σ-TCDT= 8800 pg/g	1300 pg/g 240pg/g	n.a.			Buser & Rappe 1991
Lobsters Elizabeth, Newark Bay	n.d.	2,4,6,8-TCDT 1000 pg/g Σ-TCDT= 1000 pg/g	60 pg/g 25 pg/g	n.a.			
Crabs Värö, Sweden	n.d.	2,4,6,8-TCDT 45 pg/g Σ-TCDT= 75 pg/g	40 pg/g 85 pg/g	n.a.			
Blue crabs, muscules *Callinectes sapidus* ♂, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 610 ppt	n.a.	n.a.	2,3,7,8-TCDD 50 ppt	September 1991	Cai 1994a,b
Blue crabs, muscules *Callinectes sapidus* ♀, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 480 ppt	n.a.	n.a.	2,3,7,8-TCDD 40 ppt	September 1991	
Blue crabs, muscules *Callinectes sapidus* ♂, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 260 ppt	n.a.	n.a.	2,3,7,8-TCDD 30 ppt	June 1992	
Blue crabs, muscules *Callinectes sapidus* ♀, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 270 ppt	n.a.	n.a.	2,3,7,8-TCDD 20 ppt	June 1992	
Blue crabs, hepatopancreas *Callinectes sapidus* ♂, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 300 ÷1200 ppt	n.a.	n.a.	2,3,7,8-TCDD 50 ÷ 940 ppt	September 1991	
Blue crabs, hepatopancreas *Callinectes sapidus* ♀, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 290÷10000 ppt	n.a.	n.a.	2,3,7,8-TCDD 40 ÷ 690 ppt	September 1991	
Blue crabs, hepatopancreas *Callinectes sapidus* ♂, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 310 ÷4600 ppt	n.a.	n.a.	2,3,7,8-TCDD 70 ÷ 425 ppt	June 1992	
Blue crabs, hepatopancreas *Callinectes sapidus* ♀, Newark/Raritan Bay	n.a.	2,4,6,8-TCDT 440 ÷ 4300 ppt	n.a.	n.a.	2,3,7,8-TCDD 45 ÷ 480 ppt	June 1992	
Blue crabs, hepatopancreas *Callinectes sapidus* ♂, Newark Bay	n.a.	ΣTCDT= 14800 ng/kg	n.a.	n.a.	ΣTCDD= 940 ng/kg ΣTCDF=200 ng/kg		Cooper 1993
Blue crabs, hepatopancreas *Callinectes sapidus* ♂, Sandy Hook	n.a.	ΣTCDT= 300 ng/kg	n.a.	n.a.	ΣTCDD=50 ng/kg ΣTCDF=100 ng/kg		

Blue crabs, hepatopancreas *Callinectes sapidus* ♂, Raritan Bay	n.a.	ΣTCDT= 490 ng/kg	n.a.	n.a.	ΣTCDD=90 ng/kg ΣTCDF=150 ng/kg		
Blue crabs, hepatopancreas *Callinectes sapidus* ♂, Wards Point	n.a.	ΣTCDT= 1500 ng/kg	n.a.	n.a.	ΣTCDD=210 ng/kg ΣTCDF=220 ng/kg		
Pine needles Finland Vicinity of Al smelter	present, at the LOD level	present, at the LOD level	n.d.	n.a.	ΣTCDD= 5-50 ng/kg ΣTCDF=4-15 ng/kg		Sinkkonen 1997a
Pine needles Finland vicinity of Al smelter	n.d.	n.d.		n.a.			Sinkkonen 1995a

n.a. – not analysed, n.w. – not detected

Peterman was probably the first to detect PCDTs in the environment. Peterman et al. have calculated PCDT concentrations as high as 67,000 ng/kg in soil samples from a waste pit . Electrical capacitors which contained PCBs (Aroclors 1242 and 1254) had been incinerated at this waste pit located in Crab Orchard National Wildlife Refuge. Hilker et al. have reported one of the very few observations of 2378-TeCTA in the environment . The compound 2378-TeCTA was identified in sediment samples from a sanitary sewer near a chemical plant in Niagara Falls, New York. Surprisingly high dioxin-like activity was detected in purified sample extracts.

In 1992 Benz et al. measured OCTA concentrations in soil, compost, and sewage sludge samples. The concentrations ranged from 1.0 ng/kg to 45 ng/kg. The OCTA concentrations were very low as compared to the OCDD concentrations. All samples were found to contain OCTA. The concentrations were lowest in the soil samples and highest in the sewage sludge samples.

In 1991 Buser and Rappe identified PCDTs in fly ash from two municipal solid waste incinerators and from an electric-arc furnace of a car-shredding facility. TeCDTs with three to four major and eight to nine minor isomers were detected. The 2378-TeCDT isomer was included in the TeCDTs and PeCDTs detected in the fly ash samples. The major TeCDT isomers identified in the fly ashsamples were 2367-TeCDT, 2378-TeCDT, and 2468-TeCDT. Buser et al. have estimated that the concentrations of PCDTs in fly ash were up to 55 ng/g,which was one order of magnitude below the concentrations the PCDDs and PCDFs in these samples.

In Finland in 1991 two different samples from waste combustion were found to contain TeCDTs and PeCDTs. Several TeCDTs and PeCDTs were detected in both samples. In one sample the concentrations seemed to be quite high. Later, additional stack gas samples from two different waste incinerators were found to contain TeCDTs and PeCDTs. Two samples contained the gas phase only, and two samples contained both the gas phase and the particles. One of the stack gas samples which did not contain any TeCDTs and PeCDTs were strongly suspected to contain TriCTAs and TeCTAs *[Sinkkonen, 1997]*. These samples had previously been found to contain some tri- and tetrachlorinated diphenylsulfides. The formation of organochlorine compounds in the bleaching process in pulp and paper mills has been cut down by replacement of chlorine by chlorine dioxide.

The fate of PCDTs and PCTAs released into the environment is quite unknown. For example, the environmental persistence of PCDTs due to photolysis is not well known. Hosomi et all *[2005]* and Nakai et all *[2006]* suggest that PCDTs are photolysed via sequential dechlorination of dibenzothiophene rings.

Polychlorinated dibenzothiophenes in aerobic conditions can be also oxidized. One of possible pathways is given by Kodama et all which is well documented for the compounds not chlorinated in positions 2 and 3 of benzene ring.

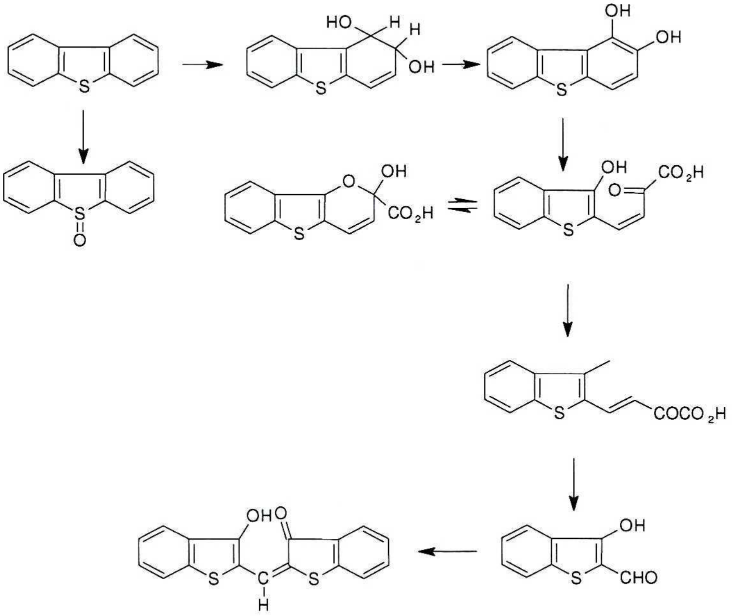
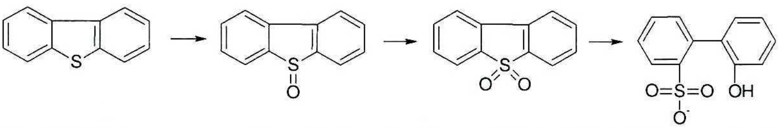


Fig. 7. Oxidative degradation of dibenzothiophene via Kodama pathway *[van Herwijnen et al., 2003; Seo J-S., 2006]*

Another one, given by Van Afterdeen *[2000]* and Bressler et all *[2000]*, with formation of adequate dibenzothiophenes oxides and dibenzothiophenes dioxides work for all unsubsituted and substituted dibenzothiophenes according to the reaction in the figure



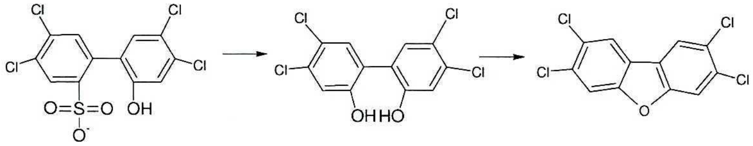
Dibenzothiophene

Dibenzothiophene-5-oxide

Dibenzothiophene-5,5-dioxide

2-sulfine -2'-hydroxybiphenyl

Fig. 8. Oxidative degradation of dibenzothiophene via Van Afferden pathway *[Van Afferden, 2000; Bressler & Fedorak, 2000]*



2'-hydroxybifenyl-4,5,4',5'-tetrachloro-2-sulfine

4,5,4',5'-Tetrachloro-2,2'-dihydroxybiphenyl

2,3,7,8-Tetrachlorodibenzofurane

Fig. 9. Proposed transformation pathway from tetrachlodihydroxybiphenysulfine to tetrachlorodibenzothiophene

Using the reaction cycle shown in Figure 8, and the fact that the SO_2 group can be easily split off and form a diol, we suggest that as a result of consecutive stages of the reaction cycle (in which a water molecule splits off), another cyclization occurs with the generation of an appropriately-chlorinated dibenzofuran molecule. This is shown in Figure 9.

Occurrence of this reaction cycle may explain the high concentrations of polychlorinated dibenzofurans and low concentrations of polychlorinated dibenzofurans in environmental samples *[Czerwiński et al., 2007; Nakai et al., 2007].*

In the anaerobic conditions chlorinated dibenzothiophenes are stable, but via enzymatic reaction of fungal haloperoxidases they can form higher chlorinated species. It may explain the presence of octachlorinated dibenzothiophenes in lechates from old landfills in concentrations one order magnitude higher than other congeners *[Dudzinska et al., 2004].*

CONCLUSIONS

The current knowledge on sulphur analogue compounds of the standard PCDD/Fs is steel very limited. Not much is known about the toxicological relevance of this group of compounds. Methods of analysis have been developed by few research groups (from Finland, USA, Germany, Poland and Japan) hence these groups also provide all data available so far on the occurrence of these compounds in environmental matrices. Following this information, particularly PCDT could be found in waste gases and fly ash of some thermal processes as well as in sewage sludge. Their concentrations are usually lower than the always accompanying PCDD/Fs; however, particular PCDT can be more and more important contaminants.

A reason for this result could possibly be found in the high SO_2 generation rate for which the previously has been identified production process is optimised for. In waste incineration SO_2 to act as an inhibiting agent for PCDD/F formation, but caused formation of polychlorinated dibenzothiophenes.

Acknowledgments

This work was supported by scientific grant No. 1 T09D 024 30 from the Polish Ministry of Science and Higher Education

REFERENCES

[1] Aittola J-P., Paasivirta J., Vattulainen A., Sinkkonen S., Koistinen J., Tarhanen J., (1996), Formation of Chloroaromatics at a Metal Reclamation Plant and Efficiency of Stack Filter in their Removal from Emission, *Chemosphere,* **32,** 99-108.

[2] Bechtler R., Stieglitz L., Zwick G., Will R., Roth W., Hedwig K., (1998), Influence of elemental sulfur on the *de-novo* synthesis of organochlorine compounds from residual carbon on fly ash, *Chemosphere,* **37,** 2261-2278.

[3] Benz T., Hagenmaier H., Lindig C., She J., (1992) Occurrence of the sulphur analogue of octachlorodibenzo-p-dioxin in the environment and investigations on its potential source, *Fresenius J. Anal. Chem.,* **344,** 286-291.

[4] Buser H-R., (1992), Identification and sources of dioxin-like compounds:
I. Polychlorodibenzothiophenes and polychlorothianthrenes, the sulfur-analogues of the polychlorodibenzofurans and polychlorodibenzodioxins, *Chemosphere,* **25,** 45-48.

[5] Cai Z., Ramanujam V.M.S., Gross M.L., Cristini A., Tucker R.K., (1994a), Levels of polychlorodibenzo-*p*-dioxins and dibenzofurans in crab tissues from Newark /Raritan Bay system, *Environ. Sci. Technol.,* **28,** 1528-1534.

[6] Cai Z., Giblin D.E., Ramanujam V.M.S., Gross M.L., Cristini A., (1994b), Mass-profile monitoring in trace analysis: Identification of polychlorodibenzothiophenes in crab tissues collected from the Newark/Raritan Bay system, *Environ. Sci. Technol.,* **28,** 1535-1538.

[7] Chen S.D., Liu H.X., and Wang Z.Y., (2007), Study of Structural and Thermodynamic Properties for Polychlorinated Dibenzothiophenes by Density Functional Theory, *J. Chem. Eng. Data,* 52, 1195 -1202.

[8] Claus E., Heininger P., Bade M., Jürling H., Raab M., (1998), Mass spectrometric identification of polychlorinated dibenzothiophenes (PCDBTs) in surface sediments of the River Elbe, *Fresenius J. Anal. Chem.*, **361,** 54–58.

[9] Cooper K. (1993), Dioxin levels in mollusks and other invertebrates in Newark Bay and Arthur Kill. Symposium on dioxin contaminated sediments in Newark Bay, Society of Environmental Toxicology and Chemistry. Hudson/Delaware Chapter, Environmental and Occupational Health Sciences Institute, Rutgers University, Feb 26.

[10] Czerwiński J., Dudzińska M.R., Rut B., (2006), Concentration of PCDDs, PCDFs and PCDTs In Bottom Ash from Domestic Heating Systems as an Effect of Fuel Composition, *Organohalogen Compounds*, **68**, 139-142.

[11] Dudzińska M.R., Czerwiński J., Rut B., (2004), Comparison of PCDD/Fs Levesl and Profiles in Leachates from „New" and „Old" Municipal Landfills, *Organohalogen Compounds* **66**, 869-874.

[12] Giesy J.P., Jude D.J., Tillitt D.E., Gale R.W., Meadows J.C., Zajicek J.L., Peterman P.H., Verbrugge D.A., Sanderson J.T., Schwartz T.R., Tuchman M.L., (1997), Polychlori-nated dibenzo-*p*-dioxins, dibenzofurans, biphenyls and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents in fishes from Saginaw Bay, Michigan, *Environ. Toxicol. Chem.*, **16**, 713-724.

[13] Hosomi M., (2005), Photodegradation and dioxin - like endocrine potential of polychlorinated dibenzothiophenes, Science Council of Asia, May 12th, 2005 – poster.

[14] Huntley S.L., Wenning R.J., Paustenboch D.J., Wong A.S., Luksemburg W.J., (1994), Potential sources of polychlorinated dibenzothiophenes in the Passaic River, New Jersey, *Chemosphere,* **29,** 257-272.

[15] Huntley S.L., Carlson-Lynch H., Johnson G.W., Paustenboch D.J., Finley B.L., (1998), Identification of historical PCDD/F sources in Newark Bay estuary surface sediments using polytopic vector analysis and radioisotope dating technique, *Chemosphere,* **36,** 1167-1185.

[16] Kobayashi S., Kitadai M., Sameshima K., Ishii Y., Tanaka A., (1999), A theoretical investigation of the conformation changing of dioxins in the binding site of dioxin receptor model; role of absolute hardness–electronegativity activity diagrams for biological activity, *Journal of Molecular Structure,* **475,** 203–217.

[17] Kopponen P., Sinkkonen S., Poso A., Gynther J., Kärenlampi S., (1994), Sulfur analogues of polychlorinated dibenzo-*p*-dioxins, dibenzofurans and diphenyl ethers as inducers of CYP1A1 in mouse hepatoma cell culture and structure-activity relationships, *Environ. Toxicol. Chem.,* **13,** 1543-1548

[18] Nakai S., Kishita S., Espino M.P., Hosomi M., (2004), Detection of polychlorinated dibenzothiophenes in Japan and investigation of their dioxin like endocrine disrupting potency, *Organohalogen Compounds*, **66**, 1495-1499.

[19] Nakai S., Kishita S., Nomura Y., Hosomi M., (2006) Polychlorinated dibenzothiophenes in Japanese environmental samples and their photodegradability and dioxin-like endocrine-disruption potential, *Chemosphere*, 67, 1852-1857.

[20] Peterson R.E., Theobald H.M., Kimmel K.M., (1993), Developmental and Reproductive Toxicity of Dioxins and Related Compounds: Cross-Species Comparisons, Critical Reviews in Toxicology 23, 283-335.

[21] Pruell R.J., Rubinstein N.I., Taplin B.K., LiVolsi J.A., D.B.R., (1993), Accumulation of polychlorinated organic contaminants from sediment by three benthic marine species, *Arch. Environ. Contam. Toxicol.,* **24,** 290-297

[22] Pruell R.J., Taplin B.K., McGovern D.G., McKinney R., Norton S.B., (2000), Organic contaminant distributions in sediments, polychaetes *(Nereis virens)* and American lobster *(Homarus americanus)* from a laboratory food chain experiment, *Marine Environ. Res.,* **49,** 19-36.

[23] Rappe C., (1994), Dioxin, patterns and source identification, *Fresenius J. Anal. Chem.*, **348,** 63–75.

[24] Sinkkonen, S.; Kolehmainen, E.; Koistinen, J.; Lahtipera, (1993), M. High-resolution gas chromatographic—mass spectrometric determination of neutral chlorinated aromatic compounds in stack gas samples. *J. Chromatogr. A,* **641**, 309-317.

[25] Sinkkonen S., (1997), PCDTs in the environment, *Chemosphere,* **34,** 2585-2594.

[26] Sinkkonen S., Paasivirta J., Lahtiperä M., (2001), Chlorinated and Methylated Dibenzothiophenes in Sediment Samples from a River Contaminated by Organochlorine Wastes, *J. Soils & Sediments,* **1,** 9-14.

[27] Sinkkonen S., Lahtiperä M., Vattulainen A., Takhistov V.V., Viktorovskii I.V., Utsal V.A., Paasivirta J., (2003), Analyses of known and new types of polyhalogenated aromatic substances in oven ash from recycled aluminum production, *Chemosphere*, **52,** 761–775.

[28] Seo J-S., Keum Y-S., Cho I-K. and Li Q.X., (2006), Degradation of dibenzothiophene and carbazole by *Arthrobacter sp.* P1-1, *International Biodeterioration & Biodegradation* 58, 36–43.

[29] Van Afferden M., Tappe D., Beyer M., Trupper H.G. and Klein J. (1993), Biochemical mechanism for the desulfurisation of coal-relevant organic sulfur compounds, *Fuel*, 72, 1635–1643.

[30] Van Herwijnen R., Wattiau P., Bastiaens L., Daal L., Jonker L, Springael D., Govers H.A.J. and Parsons J.R., (2003), Elucidation of the metabolic pathway of fluorene and cometabolic pathways of phenanthrene, fluoranthene, anthracene and dibenzothiophene by *Sphingomonas* sp. LB126, *Research in Microbiology*, 154, 199–206

[31] Wang, Z. Y.; Zhai, Z. C; Wang, L. S.; Chen, J. L.; Kikuchi, O.; Watanabe, T. Prediction of gas phase thermodynamic function of polychlorinated dibenzo-p-dioxins using DFT. *J. Mol. Struct. (THEOCHEM),* **672** (1-3), 97-104.

[32] Weber R., Hagenmaier H., Schrenk D., (1998), Elimination kinetics and toxicity of 2,3,7,8-tetrachlorothianthren, a thio analogue of 2,3,7,8-TCDD, *Chemosphere,* **36,** 2635-2641.

[33] Wiedmann, T.; Riehle, U.; Kurz, J.; Ballschmiter, K., (1997), HRGC-MS of polychlorinated phenanthrenes (PCPhen), dibenzothiophenes (PCDT), dibenzothianthrenes (PCTA), and phenoxathiins (PCPT). *Fresenius J. Anal. Chem.,* **359**, 176-188.

Received: September, 2007; accepted: June, 2008.