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Determination of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in tire fire runoff oil

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ABSTRACT

Samples of oily runoff resulting from the accidental combustion of automobile tires were analyzed for polychlorinated dibenzo-*p*-dioxins (PCDDs)and polychlorinated dibenzofurans (PCDFs). PCDDs and PCDFs were identified in each of the oil samples studied. The total levels of PCDDs and PCDFs were in the low parts per billion (ppb; 10^{-9} g of PCDDs or PCDFs per g of oil) range. In all of the samples analyzed, the total PCDD concentration was approximately 10 times greater than the total concentration of PCDFs. The most toxic PCDD, 2,3,7,8-T_4CDD, contributed only a small percentage to the overall level of the PCDDs in the oil samples.

INTRODUCTION

The formation of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in combustion processes is well documented [1]. Chlorinated PCDDs and PCDFs were first identified as a byproduct of the incineration process when they were discovered in the stack gas and fly ash of three municipal waste incinerators in the Netherlands in the late 1970's [2]. Following this initial report which linked the incineration of refuse as one source of PCDDs and PCDFs, these compounds have since been found in incinerators in North America, Europe, and Japan [3]. In fact, PCDDs and PCDFs have been detected in every municipal waste incinerator tested [4]. Emissions of PCDDs and PCDFs have also been produced from the incineration of hazardous waste [5,6] and sewage sludge [4,7]. The formation of PCDDs and PCDFs from the combustion of chemically treated [8–12] and untreated wood [13,14] has been reported, as well as from the combustion of fossil fuels [10,13,15]. The impact, however, of these sources are not recognized. Marklund *et al.* [16] have reported emissions of PCDDs and PCDFs in automobile exhaust.

In addition to incineration processes, PCDDs and PCDFs have been produced during accidental fires involving PCBs, chlorobenzenes, and other chlorinated transformer and capacitor fluids. Erickson *et al.* studied the formation of PCDDs and PCDFs from the combustion of PCBs, tri- and tetrachlorobenzenes [17,18] and tetrachloroethylene [18]. Addis [19] demonstrated that the combustion of PCB-contaminated dielectric fluids resulted in the formation of a series of PCDFs. There is no evidence to suggest that normal use of electrical equipment will produce either PCDDs or PCDFs. Thermal stress in the presence of oxygen is required for PCDD/PCDF formation.

The first recognized accidental formation of PCDDs and PCDFs from the combustion of

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chlorinated aromatic compounds in transformer fluid occurred in early 1981 [20]. The office building fire involved approximately 200 gallons (*ca.* 757 l) of transformer fluid which consisted of 65% Aroclor 1254 and 35% tri- and tetrachlorobenzenes. The soot was found to contain levels as high as 2000 ppm of PCDFs and 20 ppm of PCDDs. Other transformer and capacitor fires leading to the formation of PCDDs and PCDFs have been reported in the USA [21].

On February 12, 1990, a large fire broke out at a tire recycling dumpsite located in west central Ontario. Some thirteen million tires were involved in the blaze. The heat of the fire created a black, oily runoff. To minimize contamination of groundwater in the area, this runoff oil was collected for subsequent disposal.

The manufacturing of automobile tires involves the preparation of special polymers. Various different polymers may be used depending upon specific requirements. Chloroprene (2-chloro-1,3-butadiene) rubber is frequently used in tire manufacturing, specifically in the cover-strip, sidewall, and inner-liner portions of passenger automobile tires [22]. During combustion of the chlorine-containing material within the tires, it is possible that chlorinated aromatics would be produced. Samples of the runoff oil were submitted to the Ministry of the Environment's Dioxin Laboratory for analysis of PCDDs and PCDFs. The results of the analyses are presented in this paper.

Our laboratory is set up to routinely analyze for PCDDs and PCDFs in a variety of matrices, of which oil unfortunately is not one. Upon reviewing the literature, there were very few references citing analytical methodologies for the determination of PCDDs and PCDFs in oil or waste oil materials. Two different cleanup methods, which were initially designed for general environmental analysis of PCDDs and PCDFs, were applied to PCB-contaminated waste oil [23]. In one method, the oil sample was fractionated initially using a 50-g alumina column and the resulting fraction containing the PCDDs and PCDFs was subfractionated using a 6-g alumina column. The method yielded poor detection limits (only 100 μg of oil was loaded onto the initial column) and poor recoveries of surrogates and spikes. A more complex procedure employing five liquid–solid partitioning chromatographic columns and a variety of media (sodium sulphate, potassium silicate, silica gel, carbon impregnated glass fibres, sulphuric acid-modified silica gel and alumina) produced much better results. Up to 1 g of oil could be used, thereby lowering detection limits below 10 ppb. Good surrogate and spike recoveries were reported along with relatively little background interference.

Hagenmaier and Brunner [24] developed a procedure for the determination of PCDDs and PCDFs in motor oil samples, including used and recycled oils. Oil samples of 5 g were fractionated using alumina, a mixture of activated, acid- and base-modified silica gels, and finally on Bio-Beads S-X3. Single isomer detection limits were reported to be on the order of 0.05 μg/kg of oil. In a subsequent study involving motor oils and waste oils, a multi-column cleanup procedure was devised for the determination of PCDDs and PCDFs [25]. The method, which involved fractionation on columns containing silica gel, acid- and base-modified silica gels, florisil and alumina, was applicable to 10 g oil samples. Good analyte recoveries and reproducibility were reported. The same group also compared their method to that utilized by Hagenmaier and Brunner. They reported that the two methods produced agreeable results on duplicate samples.

Based upon the results published by the various groups cited, it appears that while there is no simple single-step cleanup procedure available, the use of a variety of chromatographic media will produce extracts amenable to analysis by gas chromatography–mass spectrometry (GC–MS).

EXPERIMENTAL

Chemicals

Silica gel (70–230 mesh) for the open column chromatographic cleanup procedure was obtained from EM Science (Darmstadt, Germany). Basic alumina was purchased from Fisher Scientific (Fair Lawn, NJ, USA). Sulphuric acid (J.T. Baker, Phillipsburg, NJ, USA) and sodium hydroxide pellets (Oxford Labs. of Canada, London, Canada) were used to prepare the acid-

and base-modified silica gel packing materials. Silver nitrate was obtained from Anachemia Chemicals (Mississauga, Canada). The preparation of the packing materials used in the column cleanup is described elsewhere [26]. HPLC-grade water (J.T. Baker) was used in the preparation of the base- and silver nitrate-modified silica gel stationary phases.

PCDD and PCDF standards were purchased from Cambridge Isotope Labs. (Woburn, MA, USA). The calibration standard used for quantitation contained five PCDDs and five PCDFs (one per tetra-, penta-, hexa-, hepta-, and octachloro congener groups) in addition to five $^{13}C_{12}$-labelled PCDDs. The surrogate standard solution used to fortify each sample consisted of the same five isotopically labelled PCDDs present in the calibration standard.

Safety

The work undertaken in this study involves the handling of toxic compounds including 2,3,7,8-T_4CDD and other 2,3,7,8-substituted PCDDs and PCDFs. Similar analyses should only be performed by specially trained personnel experienced in the handling of hazardous chemicals. The compounds studied are potential health hazards and therefore exposure to them should be minimized. Analytical laboratories must establish procedures for the safe handling and disposal of all toxic materials. All staff must be trained in these procedures and all safety measures strictly complied to.

Sample preparation

Approximately 1.5–2 g of oil per sample was weighed into a clean glass vial. Each sample was spiked with 50 μl of the surrogate fortification standard. The oil was diluted with 2–3 ml of hexane and thoroughly mixed. The dilute sample was loaded onto a chromatographic column (30 cm × 1.0 cm I.D.) containing (top to bottom) 44% (w/w) sulphuric acid–silica gel, activated silica gel, 33% (w/w) sodium sulphate–silica gel, activated silica gel, and 10% (w/w) silver nitrate–silica gel. The sample vial was rinsed with three 5-ml aliquots of hexane, each of which was added to the column. The PCDDs and PCDFs were eluted from the silica gel column using a total of 100 ml of hexane. The resulting extract was concentrated to approximately 2 ml and quantitatively transferred to the top of a column (30 cm × 0.6 cm I.D.) containing 5 g of activated basic alumina. A 100-ml portion of hexane was used to initially elute undesired components from the column and was discarded. A second fraction was eluted with 20 ml of a 10:90 (v/v) mixture of carbon tetrachloride–hexane and was discarded. The PCDDs and PCDFs were finally eluted with 30 ml of dichloromethane. Each extract was concentrated and transferred to a small conical glass vial where it was reduced to dryness under a gentle stream of high purity nitrogen gas. The final residue was redissolved with 50 μl of a solution containing 100 pg/μl of $^{13}C_{12}$-labelled H_6CDF in toluene, which is used as an instrumental performance standard.

GC–MS–MS analysis

All PCDD/PCDF analyses were performed using a Finnigan MAT TSQ 70 triple quadrupole mass spectrometer system. A Varian 3400 gas chromatograph was interfaced to the mass spectrometer using a direct capillary inlet. High-resolution GC separations were achieved using a 60-m DB-5 fused-silica capillary column, with an internal diameter of 0.25 mm and a stationary phase film thickness of 0.25 μm (J&W Scientific, Folsom, CA, USA). Ultrahigh purity helium was used as the carrier gas (Matheson Gas Products Canada, Whitby, Canada). A splitless injector system maintained at 300°C was utilized for all GC–MS–MS analyses. The GC oven temperature program was: initial temperature held at 120°C for 1 min; ramped to 250°C at 7.5°C/min; ramped to 300°C at 2.5°C/min and held for 13 min.

The triple quadrupole mass spectrometer was operated in the daughter ion mode using multiple reaction monitoring to achieve the desired selectivity. The first quadrupole region was set to selectively transmit only ions with the mass-to-charge ratio corresponding to the PCDD/PCDF molecular ions. These parent ions undergo collisionally induced dissociation (CID) in the second quadrupole region which is pressurized with approximately 3 mTorr (*ca.* 0.4 Pa) of argon gas. The third quadrupole is set to monitor two daughter ions for each PCDD/PCDF congener

group corresponding to the loss of a COCl group. A third ion corresponding to the loss of two COCl groups is monitored for the confirmation of the tetra- through octachlorinated PCDDs. Polychlorinated diphenylethers (PCPDEs) may rearrange in the mass spectrometer ion source to form PCDF molecular ions and therefore extreme caution must be taken in interpreting mass spectral data. To verify the absence of these interfering PCDPEs, the loss of HCl and Cl_2 from PCDPE molecular ions is also monitored. The ions monitored and those used for quantitation are listed in more detailed discussions of the optimization of MS–MS parameters for the determination of PCDDs and PCDFs [27,28].

RESULTS AND DISCUSSION

Five oil samples were submitted and analyzed for PCDDs and PCDFs. The results of the analyses are summarized in Table I. A large number of isomers were detected in all of the samples analyzed. Isomers from all five PCDD congener groups (tetra- through octachloro) were found to be present in each sample along with tetra-, penta-, and hexachlorinated PCDFs. The total concentration of PCDDs in each sample was approximately one order of magnitude greater than the total level of PCDFs. Although the total T_4CDD concentration was only 2–3 times the total T_4CDF concentration, the remaining PCDD congener groups were found to be present at levels 5–15 times higher than their PCDF counterparts. Similar distributions of isomers were observed for all five samples.

Congener specific analysis of 2,3,7,8-T_4CDD and the remaining 2,3,7,8-substituted PCDDs and PCDFs was performed. The results of the congener specific analyses are summarized in Table II. It should be noted that no single GC column is capable of completely isolating all seventeen 2,3,7,8-substituted PCDDs and PCDFs from the remaining PCDDs and PCDFs. Using the 60-m DB-5 column, congener specificity is only obtained for 2,3,7,8-T_4CDD plus the hepta- and octachlorinated PCDDs and PCDFs. Therefore the concentrations of the other compounds as reported in Table II actually represent the maximum possible concentrations of these

TABLE I

PCDDs AND PCDFs IN TIRE FIRE RUNOFF OIL

All concentrations expressed in parts per trillion (ppt; 10^{-12} g of PCDDs or PCDFs per g of oil). Values have been corrected for recovery of isotopically labelled surrogate standards. Superscripts indicate the number of PCDD or PCDF isomers present.

	Oil sample (sample wt. in g)				
	A (1.5)	B (1.5)	C (1.5)	D (1.6)	E (1.6)
T_4CDDs	1400^{14}	1300^{14}	1100^{14}	950^{14}	1200^{14}
P_5CDDs	2100^{12}	1800^{12}	1500^{12}	1600^{12}	1900^{12}
H_6CDDs	2200^{8}	1900^{7}	1500^{7}	1800^{7}	1900^{7}
H_7CDDs	2000^{2}	1900^{2}	1200^{2}	1400^{2}	1300^{2}
O_8CDD	3700	3200	2700	2500	3300
Total PCDDs	11 400	10 100	8000	8300	9600
T_4CDFs	610^{14}	520^{13}	480^{14}	470^{17}	510^{13}
P_5CDFs	220^{10}	180^{8}	160^{5}	290^{11}	170^{6}
H_6CDFs	140^{3}	120^{3}	56^{1}	250^{5}	53^{2}
H_7CDFs	ND(60)[a]	83^{1}	110^{1}	80^{2}	ND(50)
O_8CDF	ND(40)	34	47	ND(30)	37
Total PCDFs	970	940	850	1100	770

[a] ND = Not detected. Detection limit (in ppt) given in brackets.

TABLE II

TOXIC CONGENER ANALYSIS OF RUNOFF OIL SAMPLES

All concentrations expressed in parts per trillion (ppt; 10^{-12} g of PCDD or PCDF per g of oil). Values have been corrected for recovery of isotopically labelled surrogate standards.

Compound	Concentration in oil samples				
	Oil A	Oil B	Oil C	Oil D	Oil E
2,3,7,8-T_4CDD	53	31	23	30	33
1,2,3,7,8-P_5CDD	170	160	140	140	170
1,2,3,4,7,8-H_6CDD	68	78	30	60	57
1,2,3,6,7,8-H_6CDD	ND(10)[a]	ND(10)	ND(10)	ND(10)	ND(10)
1,2,3,7,8,9-H_6CDD	330	290	130	250	220
1,2,3,4,6,7,8-H_7CDD	950	900	570	670	630
O_8CDD	3700	3200	2700	2500	3300
2,3,7,8-T_4CDF	52	65	69	42	74
2,3,4,7,8-P_5CDF	9.6	12	11	20	12
1,2,3,7,8-P_5CDF	5.5	ND(5)	ND(8)	10	ND(5)
1,2,3,4,7,8-H_6CDF	ND(10)	ND(10)	ND(10)	73	ND(20)
1,2,3,6,7,8-H_6CDF	ND(10)	ND(10)	ND(10)	ND(10)	ND(20)
1,2,3,7,8,9-H_6CDF	ND(10)	ND(10)	ND(10)	ND(10)	ND(20)
2,3,4,6,7,8-H_6CDF	ND(10)	ND(10)	ND(10)	ND(10)	ND(20)
1,2,3,4,6,7,8-H_7CDF	ND(60)	ND(40)	ND(60)	36	ND(50)
1,2,3,4,7,8,9-H_7CDF	ND(50)	ND(30)	ND(60)	ND(30)	ND(40)
O_8CDF	ND(40)	34	47	ND(30)	37

[a] ND = Not detected. Detection limit (in ppt) given in brackets.

compounds. In other words, their true concentrations will be less than the reported values if other co-eluting isomers are present.

The contribution of 2,3,7,8-T_4CDD to the total concentration of T_4CDDs was found to be small for all samples analyzed. In fact, the concentration of 2,3,7,8-T_4CDD was found to range from 2 to 4% of the total T_4CDD concentration. The most toxic pentachlorinated PCDD, 1,2,3,7,8-P_5CDD, was estimated to constitute approximately 9% of the total P_5CDD concentration. Two toxic H_6CDDs, the 1,2,3,4,7,8-H_6CDD and 1,2,3,7,8,9-H_6CDD congeners, were tentatively identified. These two congeners contributed approximately 15% of the total H_6CDD concentration, with the latter about four times more abundant than the former. The 2,3,7,8-substituted H_7CDD was found at concentrations ranging form 570 to 950 ppt, about half of the total H_7CDD concentration in each sample. The O_8CDD congener was the predominant PCDD ranging in concentration from 2500 to 3700 ppt.

Unlike the PCDDs, the concentrations of the PCDF congener groups tended to decrease with increasing degree of chlorination. The T_4CDFs were found to account for between 42 and 66% of the total PCDF concentration. The more highly chlorinated species, the H_7CDFs and the O_8CDF, were present at low ppt levels or were not detected at all. With the exception of one sample, no 2,3,7,8-substituted H_6CDFs or H_7CDFs were identified in the oil samples analyzed. In the case of that one sample, one 2,3,7,8-substituted H_6CDF (1,2,3,4,7,8-H_6CDF) was found at 73 ppt while the 1,2,3,4,6,7,8-H_7CDF was weakly detected at 36 ppt. The highly toxic 2,3,4,7,8-P_5CDF congener was found in all five samples at concentrations ranging from 10 to 20 ppt while the less toxic 1,2,3,7,8-P_5CDF was detected at lower concentrations if at all. The highly toxic 2,3,4,7,8-P_5CDF contributed

TABLE III

2,3,7,8-T_4CDD TOXIC EQUIVALENCY FACTORS

The 2,3,7,8-T_4CDD toxic equivalency factor (TEF) is a comparison of the toxicity of a particular PCDD/PCDF isomer relative to that of 2,3,7,8-T_4CDD. For example, 1,2,3,7,8-P_5CDD is reported to have a TEF of 0.5. Therefore 10 ng of 1,2,3,7,8-P_5CDD will produce the same toxic effect as 5 ng of 2,3,7,8-T_4CDD.

Compound	2,3,7,8-T_4CDD toxic equivalency factor
2,3,7,8-T_4CDD	1.0
1,2,3,7,8-P_5CDD	0.5
1,2,3,4,7,8-H_6CDD	0.1
1,2,3,6,7,8-H_6CDD	0.1
1,2,3,7,8,9-H_6CDD	0.1
1,2,3,4,6,7,8-H_7CDD	0.01
O_8CDD	0.001
2,3,7,8-T_4CDF	0.1
2,3,4,7,8-P_5CDF	0.5
1,2,3,7,8-P_5CDF	0.01
1,2,3,4,7,8-H_6CDF	0.1
1,2,3,6,7,8-H_6CDF	0.1
1,2,3,7,8,9-H_6CDF	0.1
2,3,4,6,7,8-H_6CDF	0.1
1,2,3,4,6,7,8-H_7CDF	0.1
1,2,3,4,7,8,9-H_7CDF	0.01
O_8CDF	0.001

only approximately 7% of the total P_5CDF concentration. Similarly, the 2,3,7,8-T_4CDF was found to constitute between 9 and 14% of the total level of the T_4CDFs.

In order to estimate the relative toxicities of the oil samples, the 2,3,7,8-T_4CDD toxic equivalency concentrations were calculated using the toxic equivalency factors given in Table III. By multiplying the concentrations of the individual 2,3,7,8-substituted PCDD/PCDF congeners by the appropriate toxic equivalency factor and summing these concentrations for each sample, Table IV was generated. The 2,3,7,8-T_4CDD toxic equivalency concentrations for the five samples were found to range from 130 to 200 ppt. The predominant congeners with respect to the contribution to the total 2,3,7,8-T_4CDD toxic equivalency concentrations were 1,2,3,7,8-P_5CDD, 2,3,7,8-T_4CDD, and 1,2,3,7,8,9-H_6CDD. In all five samples, the contribution of the 2,3,7,8-substituted PCDDs accounted for approximately 90% of the total 2,3,7,8-T_4CDD toxic equivalency concentration.

The total PCDD concentrations were found to range from 8000 to 11 000 ppt while the 2,3,7,8-T_4CDD toxic equivalency concentrations for the PCDDs ranged from 120 to 190 ppt. Similarly the total PCDF concentrations ranged from 770 to 1100 ppt while the 2,3,7,8-T_4CDD toxic equivalency concentrations of the PCDFs were found to be between 10 to 19 ppt. The total concentrations of the PCDDs and PCDFs in the oil are much higher than the estimated 2,3,7,8-T_4CDD toxic equivalency concentrations. The more highly toxic 2,3,7,8-substituted congeners (those having a 2,3,7,8-T_4CDD toxic equivalency of greater than 0.1) are present at relatively low concentrations. Therefore in all cases, the

TABLE IV

2,3,7,8-T_4CDD TOXIC EQUIVALENCY OF OIL SAMPLES

2,3,7,8-T_4CDD toxic equivalency concentrations reported in parts per trillion (10^{-12} grams of 2,3,7,8-T_4CDD equivalents per g of oil).

	Oil A	Oil B	Oil C	Oil D	Oil E
PCDD contribution[a]	191	160	117	140	155
PCDF contribution[a]	10	13	12	19	13
Total 2,3,7,8-T_4CDD toxic equivalency	201	173	129	159	168

[a] PCDD contribution = total toxic equivalents from PCDDs only; PCDF contribution = total toxic equivalents from PCDFs only.

2,3,7,8-T_4CDD toxic equivalency concentrations of the PCDDs and PCDFs are less than 2% of the respective total PCDD/PCDF concentrations.

CONCLUSIONS

It is difficult to estimate the potential impact of this previously unrecognized source of PCDDs and PCDFs. Every year millions of tires are discarded worldwide. Only a very small percentage of these tires are actually recycled for other uses. Incineration is a popular method of reducing the volume of waste material. In some cases tires are actually burned as part of the fuel mixture used to generate heat for industrial operations (for example, cement kilns). Based on the findings of this study, further investigations regarding the formation of PCDDs and PCDFs through the combustion of automobile tires are clearly warranted.

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