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POLYCHLORINATED NAPHTHALENES IN SOIL, SEDIMENT, AND BIOTA COLLECTED NEAR A FORMER CHLORALKALI PLANT IN COASTAL GEORGIA, USA

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SUMMARY

Concentrations of total polychlorinated naphthalenes (PCNs) as high as 23 µg/g, dry wt, were found in sediments contaminated by the disposal of wastes from chlor-alkali processes. Concentrations of total PCNs in blue crab, fish and birds were 3- to 5- orders of magnitude less than that in sediments. The profile of PCN congeners in biota was predominated by tetra- or penta-chloronaphthalenes, while hepta- and octa-chloronaphthalenes were dominant in sediments. The 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (TEQs) estimated for PCNs in sediments and biota were greater than those reported for PCBs, PCDDs or PCDFs. These results suggest that chlor-alkali process is a source of PCNs found in the environment.

Key words: polychlorinated naphthalenes, waste disposal, marine environment

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INTRODUCTION

Polychlorinated naphthalenes (PCNs) are primarily industrial chemicals, used as dielectric fluids in transformers and capacitors and as cable insulators. PCNs were also used as engine oil additives, wood preservatives, electroplating masking compounds and as feedstocks for dye production (1). Besides their production as technical Halowax mixtures, chlorinated naphthalenes (CN) are also formed during combustion processes such as municipal solid waste incineration and in metallurgical processes (1). Several of the CN congeners are persistent, lipophilic (log K_{ow} 3.9–8.4), and bioaccumulate in the food chain and have been measured in a range of environmental media including human tissues (1, 2). Some of the 75 possible PCN congeners exhibit toxic effects similar to those of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). In this study, isomer-specific profile of PCNs was examined in soil, sediments and biota including a benthic invertebrate (blue crab), fish (striped mullet), and bird (boat-tailed grackle) collected near a former chlor-alkali plant in southeastern coastal Georgia. 2,3,7,8-TCDD equivalents (TEQs) were estimated for toxic PCN congeners and compared with those reported for PCBs, PCDDs, and PCDFs (3–5) in the same media to evaluate the relative significance of these four compound classes at this site.

MATERIALS AND METHODS

The chlor-alkali plant is located in southeastern coastal Georgia near the city of Brunswick, Georgia, USA. Details regarding the site, PCBs- and PCDDs/PCDFs- contamination in its environmental media have been described earlier (3–6). Soil samples were taken from waste disposal pits in February 1996. Surficial sediments (0–5 cm) were collected from two intertidal locations, along the contamination gradient, during low tide-one in the marsh contaminated by leaching from waste pits and by direct disposal. Sediments were freeze dried and passed through a 500 µm sieve prior to chemical analysis. Blue crabs and striped mullet were collected in March 1997, and boat-tailed grackle in August 1995 in Purvis Creek, 1 to 2 km away from the chlor-alkali plant and this creek has been receiving drains from the contaminated marsh.

Chlorinated naphthalene congeners were analyzed following the method described earlier (7) with slight modifications. Five g of soil or sediment was extracted with toluene in a Soxhlet apparatus for 20 h. The extract was concentrated and cleaned-up on a 4 g acidic-silica/silica gel (Wakogel C-200) column. Chlorinated naphthalene congeners were eluted with n-hexane (100 ml). Biological samples were extracted with 400 ml of methylene chloride and hexane in a Soxhlet apparatus for 16 h and cleaned on a acidic-silica/silica gel column similar to that described for soil samples. Chlorinated naphthalene congeners eluted with n-hexane (100 ml) were transferred to a carbon column packed with 1 g of activated carbon-impregnated silica gel. PCNs were eluted with toluene (200 ml) after an initial rinsing with 150 ml of n-hexane. A gas chromatograph (Hitachi M-80B GC) coupled with a mass spectrometric detector (GC/MSD) was used for the determination of PCN congeners. PCN homologs were determined by selective ion monitoring (SIM) at m/z 230 and 232, 264 and 266, 300 and 302, 334 and 336, 368 and 370, 402 and 404 for tri-, tetra-, penta-, hexa-, hepta- and octa-chloronaphthalenes, respectively.

RESULTS AND DISCUSSION

Concentrations of tri- through octa-CN congeners (total PCNs) in excavated soil, marsh- and creek- sediments were 17.9, 19.6 and 23.4 µg/g, dry wt, respectively (Table 1). The spatial distribution of PCN concentrations at this marsh site was different from those observed for PCBs, PCDDs, and PCDFs, which decreased by 40- to 60-fold along the contamination gradient, from excavated soil to creek sediment (3, 4). Hexa- and hepta-CN congeners contributed 70% of the total PCN concentrations in soil and sediments (Fig. 1). This was different from those found in Halowaxes 1051 or 1014. Despite the reports on the use of Halowaxes 1013 and 1014 as impregnants for carbon electrodes used in chlor-alkali process (1), a different profile of PCN homologs in soil and sediments suggests their formation in chlor-alkali process, similar to that documented for hepta- and octa-chlorodibenzofurans (5). The PCN congeners, 74, 71/72, 75, 65 and 69 were the major components in soil and sediments accounting for 37, 14, 12, 7 and 5%, respectively, of the total PCN concentrations

Table 1. Concentrations and relative composition (in parentheses; % wt) of PCN homologs in soil ($\mu\text{g/g}$, dry wt), sediments ($\mu\text{g/g}$, dry wt), and biota (ng/g, wet wt)

CN congener	Excavated soil	Marsh sediment	Creek sediment	Blue crab	Striped mullet	Boat-tailed grackle
Organic carbon (%)	2	10	5.6	NA ^a	NA	NA
Lipid content (%)	NA	NA	NA	18	1.2	4.0
Tri-CN	0.09 (<1)	0.1 (<1)	0.05 (<1)	2.36 (18)	0.52 (9)	0.24 (22)
Tetra-CN	0.64 (4)	0.65 (3)	0.53 (2)	7.18 (54)	2.28 (38)	0.23 (22)
Penta-CN	2.23 (12)	2.44 (13)	2.58 (11)	2.93 (22)	2.15 (36)	0.36 (34)
Hexa-CN	5.81 (32)	6.47 (33)	7.28 (31)	0.78 (6)	1.11 (18)	0.23 (22)
Hepta-CN	7.14 (40)	7.69 (39)	9.64 (41)	<0.04 (<1)	<0.02 (<1)	<0.06 (<6)
Octa-CN	2.03 (11)	2.26 (11)	3.35 (14)	<0.06 (<1)	<0.03 (<1)	<0.04 (<4)
Total	17.9	19.6	23.4	13.26	6.05	1.06

^aNA: Not analyzed

Table 2. Concentrations of dioxin-like PCN congeners and their toxic equivalents (TEQs; in parentheses) in soil, sediment (pg/g, dry wt) and biota (pg/g, wet wt)

Congener	IUPAC No.	TEF ^a	Excavated soil	Marsh sediment	Creek sediment	Blue crab	Striped mullet	BT grackle
1, 2, 6, 8-	40 ^b	1.65E-05	127 000	135 000	108 000	291	71	35
1, 2, 3, 6, 7-	54	1.7E-04	ND ^c	ND	ND	14 (0.002)	2.9 (0.0005)	ND
1, 2, 3, 4, 5, 6-	63	2E-03	298 000 (596)	340 000 (680)	371 000 (742)	52 (0.1)	30 (0.06)	10 (0.02)
1, 2, 3, 4, 6, 7-	66/67 ^d	2.27E-03	158 000 (358)	171 000 (387)	202 000 (458)	334 (0.76)	135 (0.31)	60 (0.14)
1, 2, 3, 5, 6, 7-	68 ^e	1.5E-04	598 000	710 000	749 000	69	252	44
1, 2, 3, 5, 7, 8-	69	2E-03	1 040 000 (2 080)	1 040 000 (2 080)	1 200 000 (2 400)	107 (0.21)	216 (0.43)	49 (0.10)
1, 2, 3, 5, 7, 8-	70	5.9E-04	ND	ND	ND	ND	ND	ND
1, 2, 3, 4, 5, 6, 7	73	1E-03	639 000 (639)	586 000 (586)	1 080 000 (1 080)	ND	ND	ND

^aFrom Ref 9. ^bCoelutes with congener 38; ^cND = Not detected. ^dPCN congeners 66 and 67 coelute and therefore an average TEF was used. ^eCoelutes with congener 64.

(see Fig. 1). Blue crab hepatopancreas contained the greatest concentrations (13.3 ng/g, wet wt) followed by striped mullet (6.05 ng/g), and grackle (1.06 ng/g) muscle tissues (Table 2). TetraCN congeners accounted for the greatest proportion in blue crab and striped mullet whereas pentaCNs predominated in grackle (see Table 1). The profile of PCN congeners in biota did not resemble those found in greatly chlorinated Halowax mixtures I014 and I051. Although, the pattern of PCNs in blue crab hepatopancreas matched with those of Halowax I013, this does not necessarily mean exposure to this technical mixture because neither sediments nor other biological samples contained similar PCN distribution. Lower chlorinated naphthalenes are more water soluble and therefore are more bioavailable than higher chlorinated naphthalenes. Despite the predominance of hepta- and octa-CNs in sediments, these congeners were not accumulated in the biota. Steric hindrance in the uptake of large molecules, with an effective cross section (ECS) of $>9.5 \text{ \AA}$, through biological membranes has been suggested. Occurrence of heptaCN congeners has been reported in biota, although at a relatively lesser concentrations. Further, PCNs tend to bind strongly to sediment organic carbon and therefore, their bioavailability is limited in organic-rich sediments.

The 2,3,7,8-TCDD equivalents (TEQs) were estimated for the active PCN congeners in soil, sediment and biota collected at the chlor-alkali plant and the results were compared with those reported for PCBs and PCDDs/DFs (see Table 2). HexaCN congener 69 and heptaCN congener 73 contributed to greater than 60% of the TEQs in soil and sediments. The TEQs for PCN congeners 66/67, 54, 63, and 69 in biota were 0.25–1.1 pg/g, wet wt, which were greater than those of the TEQs reported for non-ortho PCBs, PCDDs and PCDFs in blue crab, striped mullet, and boat-tailed grackle from the same location (5). The results suggest that PCNs are potentially important toxic contaminants formed in the chlor-alkali process. The contribution of PCNs to dioxin-like toxicity in environmental media near chlor-alkali plants may be greater than the contribution due to PCBs, PCDDs or PCDFs.

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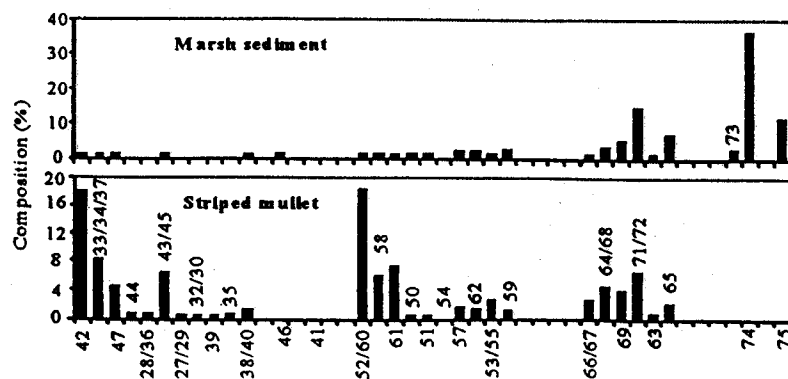


Fig. 1. Relative composition (%) of PCN congeners to total PCN concentrations in sediment and fish collected near a former chlor-alkali plant.

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THE EVALUATION OF DIOXIN EMISSIONS FROM PILOT SCALE INCINERATION OF ORGANOCHLORINE COMPOUNDS

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SUMMARY

Formation of the dioxins was investigated in case of two fuel types (kerosene-dichlorobenzene and kerosene-dichloroethane) on a pilot scale liquid waste incinerator. It was determined the effect of the molecule structure (aromatic, aliphatic) and Cl content (1, 3 and 6 %) of the liquids and the combustion parameters (O₂ content, residence time and temperature). In some experiments particulate matters (fly ash and soot) were injected. The measured dioxin concentrations ranged up to 160 ng/Nm³ or till 10 ng/Nm³ TEQ, except at addition of soot where extremely high dioxin concentrations (up to 750 ng/Nm³, or 30 ng/Nm³ TEQ) were measured. Main conclusions of the experiment are: The incineration of aromatic chlorinated products produce almost 10 times higher dioxin concentrations than the aliphatic ones. A relatively low dioxin concentration is caused at low (1 to 3 %) feed Cl contents while over a threshold value of more than 3 % Cl intensifies sharply the dioxin formation. The dioxin generation can be characterized with concentrations measured at 600-650 °C. Dioxin toxicity reduction occurs when cooling down to 200-250 °C. Changes between these sampling temperatures can be explained mostly by sorption phenomena occurring between dioxin content of flue gases and solid deposits.

Key words: dioxin, combustion, organochlorine, toxicity

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INTRODUCTION

Dioxin emission is one of the most important environmental problem being most often connected to combustion processes. High dioxin emissions can be generated by the incineration of municipal or hazardous industrial wastes containing PVC, chlorinated spent solvents, phenols, pesticides of PCBs.

Many publications have appeared on the problems of dioxin formation mechanism, the role of combustion parameters but the results still look very contradictory. Two main formation pathways are suggested: de novo synthesis (1, 4, 5) and formation from precursor compounds (3) together with numerous further hypothesis based on the influences of dislocated graphite crystal structure, the effect of flue gas cooling to 200-250 °C, and on the preferential adsorption of dioxines on solid surfaces.

While "in vitro" experimental research looks to be far from the complexity of the real factors, full scale industrial observations rarely gave consistent conclusions, often limited to describing phenomena like "memory effect" (7, 8).

In a cooperative research project realized with TIRU S.A. a major European waste incineration company, this study takes profit from the capabilities of the liquid waste pilot incinerator of the Environmental Pilot Laboratory of the Technical University of Budapest.

MATERIALS AND METHODS

The equipment of max. 20 kg/h capacity assure strictly controlled experimental conditions, the simultaneous measurement and computer data acquisition of many operational parameters and component concentrations. An ease of controlled change in wide range of parameters (flue gas residence time of 1 to 8 s, air excess factor between 0 and 100 %, temperature of 800 to 1350 °C), the possibility of cleaning its major elements and the highly developed gas scrubber system assures best conditions. A new heat exchanger has been inserted into the flue gas line to locate sampling ports M1 and M2 to temperatures being most relevant to dioxin formation (Fig. 1).

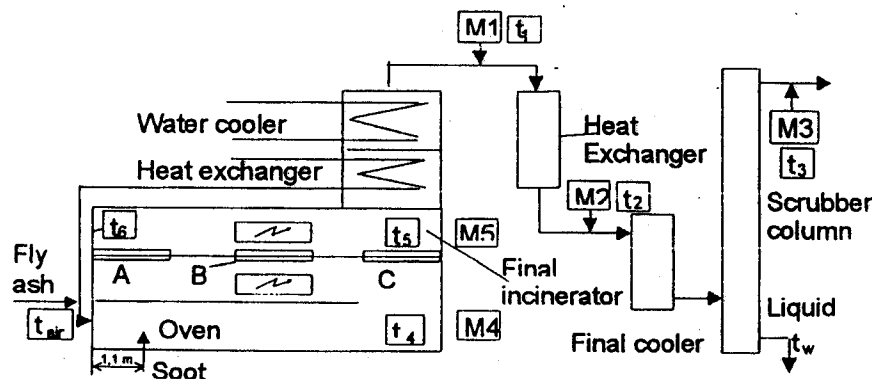


Fig. 1. The pilot liquid waste incinerator

