

Congener-Specific Analysis of Polychlorinated Naphthalenes in the Waste Samples

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Introduction

Polychlorinated Naphthalenes (PCNs) are the compounds formed by chlorine substitution of naphthalene and constituted from 75 congeners. Since PCNs are chemically and thermally stable like polychlorinated biphenyls (PCBs), they are used as insulation oils, preservatives, intermediates for dyes, additives for machine oils or rubber products, and flame retardants^{1, 2}. Typical PCN formulations are Halowaxes (Koppers, US), Nibren waxes (Bayer, Germany), Seekay wax (ICI, UK), and Clonacire wax (Prodelec, France). The world-wide production of PCNs is estimated as 150,000 tons². Because of their toxicity and environmental persistence, production and use of PCNs were regulated in many countries. However, PCNs once used as formulations or formed by combustion processes are frequently found in the environmental samples yet²⁻⁵. Since PCNs formerly used are possibly contained in the wastes, we analyzed PCNs in rubber samples collected from municipal wastes. Moreover, PCN waxes were accidentally imported to Japan and synthetic rubber (Neoprene FB) was produced using them within 1998 – 2000⁶. This synthetic rubber containing PCNs was used for manufacturing printer belts for IT equipments or caulking for cars. When these IT equipments will be discarded at the end of their lives, PCNs will be mixed in recycled materials and municipal wastes. To estimate the sources of PCNs in these waste samples, congener profiles of the waste samples were compared with those of Halowax formulations⁷, Neoprene FB, fly ashes, and sediments.

Materials and Methods

As waste samples, 19 kinds of rubber products from municipal wastes, 9 kinds of refuse derived fuel (RDF), 3 kinds of automobile shredder residue (ASR) were analyzed. In order to compare the levels and congener profiles of PCNs, 21 kinds of printer belts, 1 kind of Neoprene FB, 3 kinds of fly ashes, 5 kinds of sediments were also analyzed. Seven kinds of Halowax formulations (HW1000, 1001, 1013, 1014, 1031, 1051, 1099) were purchased from Foxboro Co. PCNs standard solution was PCN-MXB (Wellington Lab.). PCNs clean-up spike solution was prepared from ¹³C-labeled PCN congeners (PCN #27, 42, 52, 64, 67, 73, 75, from Cambridge Isotope Lab.). All solvents were of dioxin analysis grade from Kanto Chemicals.

Samples were extracted by Soxhlet extraction with toluene. The extract was concentrated and then solvent was changed to hexane. For the analysis of sediment sample, sulfur was removed by soaking copper wire in the extract. The extract was spiked with clean-up spike solution and then loaded to a multi-layer silica gel column (10% AgNO₃-silica gel/ 22% H₂SO₄-silica gel/ 44% H₂SO₄-silica gel/ 2% NaOH-silica gel). PCNs and other organochlorine compounds were recovered with 220ml of hexane. The eluent was concentrated and then loaded to an activated-carbon cartridge column (Carboxen, Supelco). The cartridge column was washed with 200 ml of 25% dichloromethane/hexane and then recovered by reverse flush with 120ml of hot toluene. The eluent was concentrated to 100 µl and then measured by HRGC/HRMS.

Operating conditions of HRGC/HRMS were as follows;

GC/MS: Agilent 6890GC/Micromass AutoSpec 3000, Capillary column: J&W Ultra 2 (25m x 0.20mm, df=0.33µm), Carrier gas: He (1.0ml/min), Injection port temperature: 200 °C, Injection: Splitless, Injection volume: 1µl, Oven temperature: 110°C (2min)-8°C/min-200°C-2°C /min-230°C(3min)-8°C/min-300°C, Interface temperature: 280°C, Mass resolution: 10,000, Ionization: EI (38V), Ionization chamber temperature: 250°C, Ionization current: 500µA, Acceleration voltage: 8kV.

Results and Discussion

Total PCNs levels in the waste and related samples

Quantitation results of total PCNs are shown in Table 1. PCNs were found from all samples. The levels of total PCNs were 3.1 – 130 ng/g for rubber wastes, 3.4 – 86 ng/g for RDF samples, 26 - 40 ng/g for ASR samples, 0.89 – 2,000,000 ng/g for printer belts, 90 – 700 ng/g for fly ash samples, 0.78 - 74 ng/g for sediments. Among the rubber products, mat 1 (130 ng/g), Cleaner hose (110 ng/g), and leather shoe sole (85 ng/g) were slightly contaminated with PCNs. Among the printer belt samples, belt 21 (2,000,000 ng/g), 10 (97,000 ng/g), and 4 (9,100 ng/g) were highly contaminated. Concentration of PCNs in Neoprene FB was 36,000,000 ng/g and comparable to the quantitation result (45,010,000 ng/g) reported by Yamashita et al ⁶.

Table 1 Total PCNs concentrations in the waste and related samples

Sample	PCNs (ng/g)	Sample	PCNs (ng/g)	Sample	PCNs (ng/g)	Sample	PCNs (ng/g)	Sample	PCNs (ng/g)
Floor sheet	30	Balloon	43	RDF 8	86	Belt 9	98	Neoprene FB	36,000,000
Rubber boat	45	Rubber band 1	16	RDF 9	40	Belt 10	97,000	Fly ash 1	700
Car tire	15	Wrist band	38	ASR 1	40	Belt 11	4,100	Fly ash 2	90
Bicycle tire tube	12	Rubber band 2	21	ASR 2	30	Belt 12	3.9	Fly ash 3	160
Cord	14	Eraser	48	ASR 3	26	Belt 13	20	Sediment 1	1.0
Hose	7.9	Condom	3.1	Belt 1	19	Belt 14	15	Sediment 2	0.78
Mat 1	130	RDF 1	47	Belt 2	8.6	Belt 15	79	Sediment 3	74
Mat 2	30	RDF 2	32	Belt 3	3.5	Belt 16	20	Sediment 4	48
Cleaner hose	110	RDF 3	38	Belt 4	9,100	Belt 17	0.89	Sediment 5	68
Sandal	5.5	RDF 4	11	Belt 5	5.4	Belt 18	230		
Sneaker sole	19	RDF 5	12	Belt 6	670	Belt 19	21		
Leather shoe sole	85	RDF 6	3.4	Belt 7	110	Belt 20	8.7		
Bag	17	RDF 7	7.3	Belt 8	140	Belt 21	2,000,000		

Congener profiles of PCNs in the waste and related samples

Congener profiles of PCNs in some waste and related samples are shown in Fig. 1. Correlation analysis results of these samples and the Halowax series are also denoted in below. Chlorine content in the Halowax series increases in order of HW1031, 1000, 1001, 1099, 1013, 1014, 1051. Highly chlorinated Halowaxes more contains highly chlorinated PCN congeners than lower chlorinated Halowaxes. HW1000 and 1031 which contained mono- and diCNS at high proportions were used as lubricants or woods impregnants. HW1001 and 1099 which contained tri- and tetraCNS at high proportions were used as insulators for condensers. HW1013 and 1014 were used as insulation oils which contained tetra- through hexaCNS at high proportions. Congener patterns of the waste products were also compared to the pattern of Neoprene FB. Congener profile of Neoprene FB is similar to HW 1099 or 1001 (Fig. 1).

(1) Rubber products: Rubber products which congener profiles were similar to the one of HW 1001 were floor sheet (correlation coefficient: 0.98), rubber boat (0.92), cleaner hose (0.93), eraser (0.96). Congener profile of mat 2 was similar to the one of HW 1031 (0.92). Congener patterns of leather shoe sole (0.93) and wrist band (0.91) were similar to the one of HW 1013. Congener patterns of balloon (0.99) and rubber band 1 (0.95) were similar to the one of HW 1000. Rubber products, which PCN congener patterns were similar to the one of HW 1099, were floor sheer (0.97), rubber boat (0.89), bicycle tire tube (0.87), cleaner hose (0.84), sneaker sole (0.84), leather bag (0.82) and

eraser (0.90). These results suggest that some rubber products may be mixed with PCNs formulations used earlier or contaminated in the recycling processes.

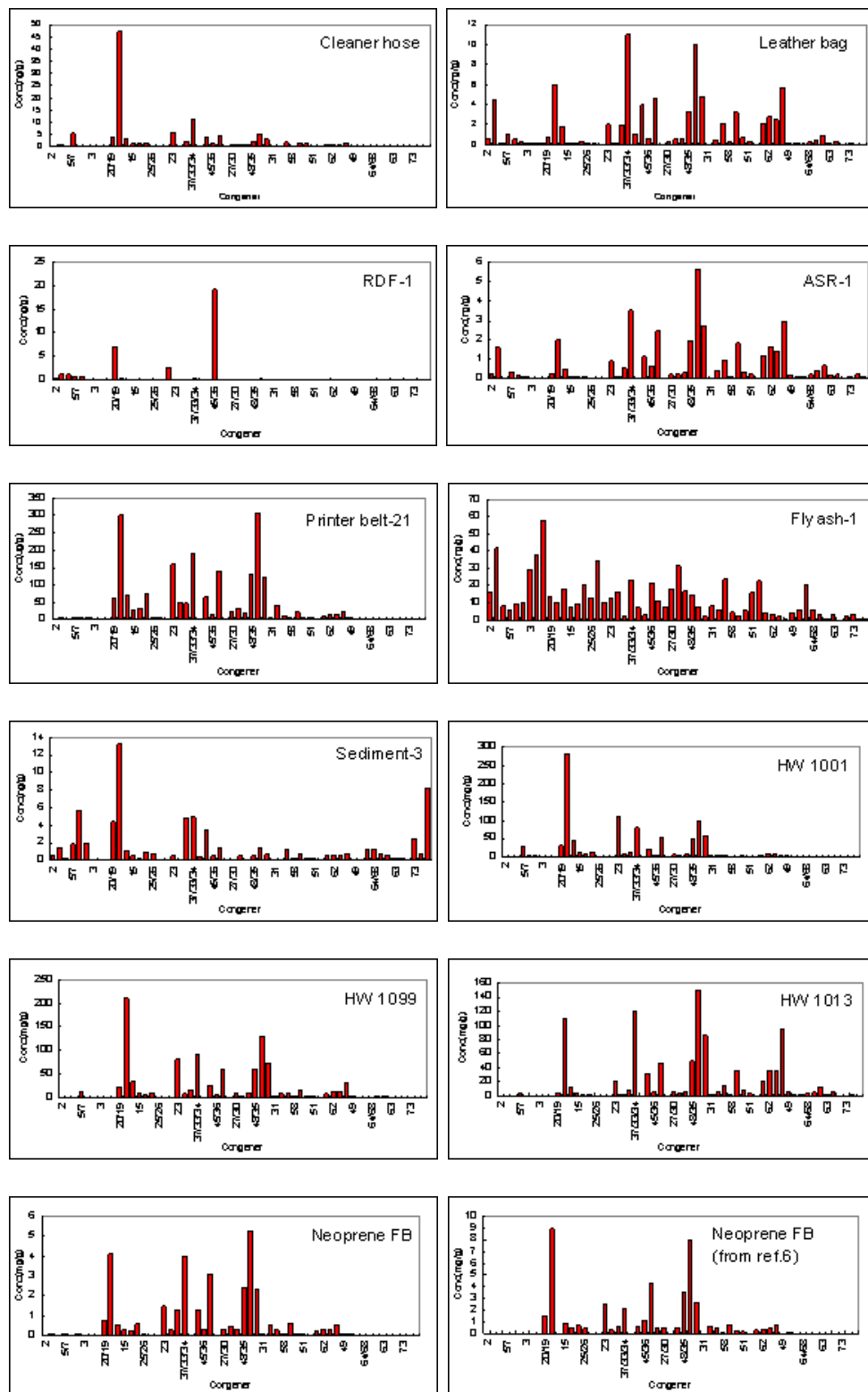


Fig. 1. Congener profiles of PCNs in waste and related samples

(2) RDF: RDF samples analyzed in this study exhibited unique congener profiles which the abundance of #45/36 (1,3,6,8-/1,2,5,6-), #20/19 (1,3,6-/1,3,5-), and #23 (1,4,5-) was extremely high (Fig. 1). These congeners are thought as combustion origin^{4, 5}, but similarity of congener profile of RDF samples to fly ash samples was small (<0.19). Similarity of congener patterns to HWs and rubber products was also small (<0.37). Among RDF samples, congener pattern were quite similar to each other.

(3) ASR: Congener profile of ASR was similar the one of to HW1013 (0.94). Similarity of congener profiles to RDF and fly ash samples was small.

(4) Printer belts: Congener profiles of belt 1 (0.81), 4 (0.97), 10 (0.81), 11 (0.82), 13 (0.86), 14 (0.90), 16 (0.90), 20 (0.88), and 21 (0.95) were similar to the one of HW1099. Congener profiles of belt 4 (0.93), 5 (0.90), 11 (0.92), 16 (0.96) were similar to the one of HW1001. Belt 10 (0.90) was similar to HW1013. Belt 2 (0.84), 7 (0.99), 17 (0.97) were similar to the one of HW1031. Congener patterns of belt 4 (0.98), 10 (0.97), and 21 (0.97) were also similar to the one of synthetic rubber, Neoprene FB. From these results and high contamination levels, belt 4, 10, and 21 should be manufactured from PCN contaminated synthetic rubber.

(5) Fly ash: Congener profiles of fly ash samples were quite complicated and thought to be combustion origin^{4, 5}. Congener patterns of fly ash samples were different from those of Halowaxes, rubber products and sediments (<0.3), while they were similar to each other (0.76 – 0.85).

(6) Sediments: Congener profiles of sediments SD 3 – 5 which were collected from the same canal were similar to each other (>0.99). Congener profile of SD 1 was similar to the one of HW 1031 (0.95). Congener patterns of the other sediments were somewhat similar to HW 1001 (0.61 – 0.77). Similarity to the rubber products, RDF, ASR, and fly ash was low. Large parts of PCNs in these sediments may attribute PCN formulations formerly used.

From these results, it is revealed that some of printer belts and municipal wastes in Japan contain PCNs from PCN formulations.

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