DECHLORANE PLUS IN FISH FROM URBAN-INDUSTRIAL RIVERS

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Abstract
The chlorinated flame retardant, Dechlorane Plus (DP), was measured in fish samples collected in 2008 from 22 river sites across Korea. Concentrations of the DP isomers ranged from 0.61 to 126 ng/g lipid, with a mean concentration of 24.5 ng/g lipid, which was relatively higher than those of the Great Lakes. The relatively high concentrations of DP in fish samples provided the DP isomers were bioavailable and bioaccumulative regardless of their high molecular weight and high log K_{ow} value. The mean DP concentrations of 15 urban sites (36.1 ± 35.3 ng/g lipid) were about 25 times greater than those measured in 7 rural sites (1.4 ± 1.0 ng/g lipid). The results suggested that DP exposure of fish is related to urbanization activity, and specific industrialized urban areas could be significant source regions of DP, even if without a DP manufacturing facility in Korea. The mean f_{anti} value for the entire samples was 0.69 ± 0.054, and the mean f_{anti} value for urban samples (0.67 ± 0.060) was significantly lower than those of technical DP standard (0.75) (p=0.032). This observation suggests the different bioavailablity of the DP isomers and enrichment of syn-DP isomer in fish samples.

Introduction
Dechlorane plus (DP, $C_{18}H_{12}Cl_{12,}$ Figure 1) is a chlorinated flame retardant which was manufactured as a substitute for Dechlorane (also called Mirex, $C_{10}Cl_{12}$) by Hooker Chemical (now known as OxyChem, Niagara Falls, NY) in the mid-1960s[1]. The major applications for DP are an additive flame retardant that is compatible with a range of polymers used for electrical wires and cable coatings, computer connectors, and plastic roofing materials. The flame retardant has been used for more than 40 years, with annual production being estimated to be as high as 10 million pounds, and has been sold worldwide including North America, Europe, and Asia [2,3]. DP is unregulated for use, but the United States EPA lists it as a high-production-volume (HPV) chemical, and Environment Canada also lists it on Canada's Domestic Substances List (DSL). According to the DP report by OxyChem to the EPA HPV challenge program, DP showed ecotoxicological effects in fish and may affect sediment bearing organisms due to its adsorptive properties based on the laboratory test [1].
The DP isomers have been detected in biota samples from the North American Great Lakes indicates that DP can be bioaccumulated and biomagnified regardless of its high molecular weight and very high log K_{ow} value[1,4,5,6,7]. The relatively low DP concentrations were observed in archived fish (walleye) samples from Lake Erie at levels in the range of 0.14-0.91 ng/g lipid[1]. Tomy et al. examined that the bioaccumulation of the DP isomers in archived food web samples from Lake Winnipeg and Lake Ontario[4]. Concentrations of the DP isomers in fish from Lake Ontario (0.015-1.554 ng/g lipid) were much higher than those of Lake Winnipeg (0.035-0.816 ng/g lipid). In addition, Gauthier et al. reported that several flame retardants including DP were accumulated in maternal herring gull via their aquatic environment and food web, and transferred during ovogenesis to their eggs[6,7]. However, biotic monitoring data of the DP isomers were limited and the environmental degradation fate of the DP was not determined[8]. Moreover, limited information of the DP available for biological exposure were mostly focused on the Great Lake regions because there is a manufacturing plant of the DP. In this paper, we report DP levels and isomeric composition in fish collected from rivers close to urban/industry areas and rural areas in Korea.

Materials and Methods
Sampling: All fish samples were collected in late July to early October 2008. The samples were collected from 18 rivers running through the major industrial complexes, and the four major rivers in Korea. Three major industrial complexes are the Ulsan-Onsan industrial complexes (I_A), the Shihwa-Banwol industrial complexes (I_B), and the Yeosu-Gwangyang industrial complexes (I_C). The four major rivers are Han river (R-19), Nakdong river (R-20), Geum river (R-21), and Yeongsan river (R-22), which present the background rural areas. The samples were freeze-dried, transferred to a Teflon-lined capped glass jar, and frozen until analysis.

Sample analysis: Approximately 1 g of freeze-dried fish tissue were spiked with a surrogate standard ($^{13}C_{12}$-Mirex), and extracted with dichloromethane using a Dionex ASE 200 (Dionex Co., CA, USA) accelerated solvent extraction (ASE). Lipid was removed using gel permeation chromatography packed with 60 g of Biobead SX-3 (Bio-Rad Laboratories, USA). Further purification was achieved on a column of silica gel (Merck, Germany) and Florisil (Aldrich, USA). Before the analysis, the samples were reconstituted with the isotopically labeled recovery standard. DP in fish samples was analyzed by gas chromatography-high resolution mass spectrometry (GC-HRMS) on an Agilent 6890 N gas chromatography coupled to a JEOL 800D mass spectrometry with the electron impact (EI) mode.

Chemicals: Technical grade DP (100 μg/mL, in nonane) was supplied by Cambridge Isotope Laboratories (Cambridge, MA, USA), and is comprised of two isomers, syn- and anti-DP. The mass labeled $^{13}C_{12}$-mirex and $^{13}C_{12}$-PCB 70 were purchased from Cambridge Isotope Laboratories (Cambridge, MA, USA), and were used as internal surrogate standard and recovery standard, respectively. The solvents and chromatographic materials were all of pesticide-analysis grade.

Results and Discussion

Spatial and Temporal Concentrations of *syn*- and *anti*-DP

Concentrations of DP isomers in fish samples are given in Table 1. The DP isomers were detected in all fish samples (n=22) collected in 2008. The observation indicated that DP was accumulated in various fish species with relatively high concentrations, even though without a DP manufacturing facility in Korea. The samples consisted of five kinds of fish species from 18 river sites close to three different industrial complexes and from rural river sites of the four major rivers. Concentrations of DP isomers ranged from 0.61 to 126 ng/g lipid, with an average concentration of 24.5 ng/g lipid. In all samples, concentrations of *anti*-DP were consistently greater than that of the *syn*-isomer. The average concentrations of DP in I_A (n=7), I_B (n=8), I_C (n=3), and R (n=4) were 28, 43, 1.2, and 1.6 ng/g lipid, respectively. The I_A area is within the Ulsan metropolitan city and the Ulsan–Onsan industrial complex which has petrochemical plants, automobile plants, and shipbuilding plants. Relatively high concentrations of DP were measured in fish from I_A-1 to I_A-5 where inner sites of the Ulsan metropolitan and close to the industrial complex. The I_A-6 and I_A-7 are semi-rural sites showed relatively low DP concentrations compared to I_A-1 to I_A-5. The I_B is highly industrialized/populated area, surrounded with the Seoul metropolitan areas, and has the Shihwa-Banwol industrial complex which composed of numerous plants for chemicals, polymers, and electronics. Exceedingly high concentrations of DP were observed in fish samples from the I_B sites with ranging from 7.6 to 80 ng/g lipid. It was suggested that DP exposure to fish is related to urbanization and industrial activity. However, I_C showed the relatively low concentrations of DP were observed in fish samples. It could be explained by the location of I_C is rural, although the site is the industrial complex has steelmaking company and petrochemical plants. We also collected fish samples from rural sites of the four major rivers across Korea (R19-R22). The DP concentrations from the R19-R22 showed the relatively low concentrations compared to the urbanized sites (I_A and I_B). The results indicated that specific industrialized and populated urban area could be a specific-region source of flame retardants such as DP or PBDEs

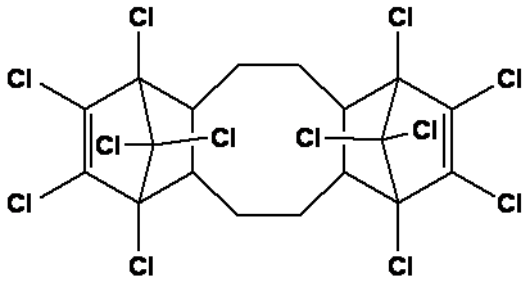

Figure 1. Structure of Dechlorane Plus

Table 1. Concentrations of DP isomers (ng/g lipid) and fraction of *anti*-DP

Site	samples	*syn*-DP	*anti*-DP	ΣDP	f_{anti}
I_A-1	common mullet	9.8	13	23	0.57
I_A-2	common mullet	10	17	27	0.63
I_A-3	common mullet	29	97	126	0.77
I_A-4	common mullet	3.6	10.7	14.2	0.75
I_A-5	oriental goby	0.98	2.7	3.7	0.74
I_A-6	common mullet	0.74	1.4	2.1	0.65
I_A-7	steed barbel	0.56	1.4	2.0	0.72
I_B-8	oriental goby	4.6	10	15	0.69
I_B -9	oriental goby	5.2	13	18	0.71
I_B -10	common mullet	19	34	53	0.64
I_B -11	oriental goby	30	38	68	0.56
I_B -12	oriental goby	2.4	5.2	7.6	0.68
I_B -13	common mullet	25	55	80	0.69
I_B -14	common mullet	18	36	54	0.66
I_B -15	common mullet	16	31	47	0.66
I_C -16	temperate sea bass	0.25	0.56	0.80	0.69
I_C -17	common mullet	0.45	1.1	1.6	0.72
I_C -18	oriental goby	0.36	0.84	1.2	0.70
R-19	crusian carp	0.90	2.7	3.6	0.75
R-20	crusian carp	0.32	0.68	1.0	0.68
R-21	crusian carp	0.32	0.95	1.3	0.75
R-22	crusian carp	0.17	0.44	0.61	0.72

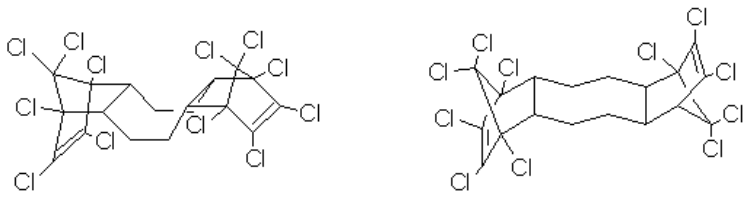

Figure 2. Structures of syn- and anti-DP

Isomeric Profiles

The technical DP has two isomers: syn- and anti-DP. The fractional abundance of the anti-isomer (f_{anti}) is calculated by dividing the concentration of the anti-DP isomer by the sum of the concentrations of *syn*- and *anti*-DP isomers. The mean f_{anti} was calculated to be 0.75 (n=3) of the technical DP standard (CIL) in our laborotary, which is similar to that reported by Hoh et al. (2006) (0.75-0.80), Qie et al. (2007) (0.75), and Gauthier et al. (2009) (0.75-0.77), but is apparently higher than that reported by Tomy et al. (2007) (0.65)[1,3,4,7]. The mean f_{anti} value for the entire samples in this study was 0.69 ± 0.054. The mean f_{anti} value for the urban samples (I_A and I_B) (0.67 ± 0.060) was lower than those of the rural samples (I_C and $_R$) (0.71 ± 0.025), but statistically not significant. The mean f_{anti} value for the urban samples was significantly lower than those of technical DP standard (0.75) ($p<0.032$). The relatively low f_{anti} value was observed in biological samples suggests that the bioavailability or biodegradation of the two isomers could be different. Hoh et al. reported that the mean fraction was 0.60 ± 0.05 in archived fish samples from Lake Erie, and suggested the structural conformation of the anti-DP isomer may be

more reactive to biological attack[1]. Tomy et al. also showed that the f_{anti} value for several fish species from Lake Ontario was 0.51-0.58, suggesting stereoselective enrichment of the syn-DP isomer relative to the commercial mixture[4]. The bioaccumulation parameters of the DP isomers from dietary exposure experiment using juvenile rainbow trout were clearly different in the bioaccumulation potentials of the two isomers of DP[5]. The average uptake rate for syn-DP was statistically greater than those of the anti-DP, which were calculated to be 0.045 ± 0.005 and 0.018 ± 0.002 nmol/day, respectively. The mean f_{anti} was measured as 0.69 ± 0.08 in the herring gull egg pools from Great Lakes, which also slightly lower than the mean f_{anti} of the commercial product (0.75-0.77)[7].

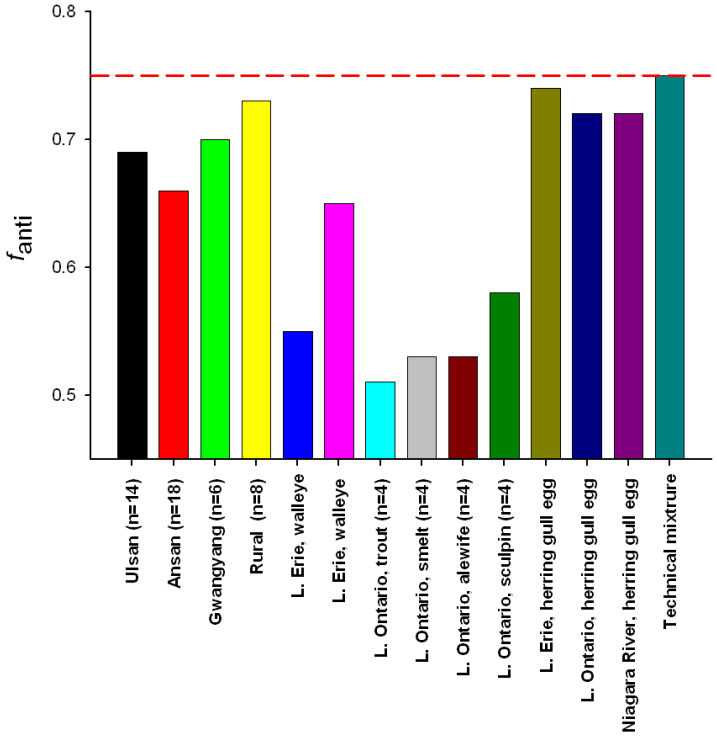

Figure 2. The f_{anti} values in fish, herring gull eggs, and DP standard

Acknowledgements
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