

BIOACCUMULATION OF DIOXINS IN TERRESTRIAL FOOD CHAIN: CONCENTRATIONS OF DIOXIN CONGENERS AND TROPHIC LEVEL

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Abstract

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and non- and mono-*ortho*-substituted polychlorinated biphenyls (dioxin-like PCBs) was analyzed in earthworms, plants, insects, field mouse and birds collected in Kanagawa Prefecture and their accumulation in the terrestrial ecosystem was studied. TEQ was highest in raptor species and followed by mouse liver, other birds, earthworms, plants and insects. Furthermore, the relationships between concentrations of PCDD/F congeners and trophic level based on nitrogen stable isotope ratio ($\delta^{15}\text{N}$) were examined. The results showed that 2,3,7,8-TeCDD/F concentrations were elevated along with trophic level rising. On the other hand, OCDD/F concentrations were not significantly elevated along with trophic level.

Introduction

It has been revealed that persistent organic pollutants (POPs) emitted in the past still remain in environment, and are accumulated through food web^{1,2}. In addition, it has been reported that accumulated POPs give adverse effect on wildlife³. In aquatic food web, it has been observed that 2,3,7,8-TeCDF concentration increased with rising trophic level while OCDD concentration decreased⁴. However, few studies have been conducted on terrestrial food web. Therefore, in this study, accumulation of dioxin was monitored for terrestrial organisms. In geochemistry, stable isotope ratio has been used as an indicator of trophic position. Generally, it has been known that stable nitrogen isotope ratios ($\delta^{15}\text{N}$) in predator animals are higher than in those in the preys by about 3~4‰⁵, based on which, relative trophic position of an animal in the food web can be estimated. In this study, the relationships between concentration of dioxins and stable isotope ratio in terrestrial animals were examined and relationships between PCDD/Fs and trophic level were reported.

Materials and Methods

Sample Collection:

Earthworm, plant, insect, and field mouse samples were collected from the fallow in Kanagawa Prefecture, Japan. Bird samples were collected by Kanagawa Prefectural Nature Conservation Center, Kanagawa, Japan, which is a re-habilitation center for injured wild birds. Bird samples were collected throughout the Kanto region, Japan (Figure 1). Earthworms (*Megascolecidae* and *Lumbricidae*) were collected in August and October 2005, May and November 2006. Plants (*Erigeron philadelphicus*) and insects (*Atractomorpha* and *Oxya japonica* and *Patanga japonica*) were collected in November 2006. Field mouse (*Apodemus speciosus*) was collected in December 2006. Earthworm, plant, insect samples were collected by hand while field mouse sample was collected by a trap. The birds that died after the accident or sickness were provided for analysis. The samples consisted of Northern Goshawk (*Accipiter gentilis*), Peregrine Falcon (*Falco peregrinus*), Japanese Sparrowhawk (*Accipiter*

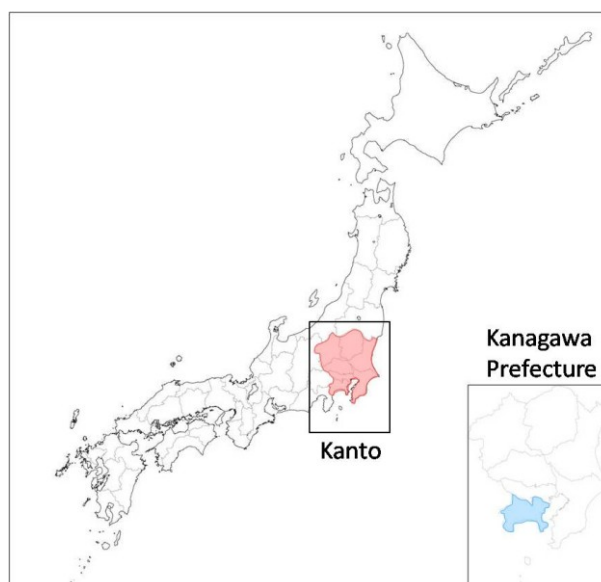


Figure 1 The location of Kanto region and Kanagawa prefecture, Japan

gularis), Brown-eared Bulbul (*Ixos amaurotis*) and Scaly Thrush (*Zoothera dauma*). All the samples were kept at -30°C until analysis.

Dioxin analysis:

Whole body of earthworm, insect, and plant were used for analysis. A liver of a field mouse and muscles of birds were also used for analysis. All samples were freeze-dried prior to analysis. Details of the analytical procedures were based on the official method established by Ministry of the Environment (MOE) of Japan⁶. The ¹³C-labeled internal standards were added to all samples and then extracted in a Soxhlet apparatus with distilled toluene for 16 hours. The extracts of all samples were concentrated to 10 ml. And 1ml of the concentrate was used for measuring the lipid contents by gravimetric method. Multilayered silica gel chromatographic column and activated carbon column were used as cleanup procedures. Finally, ¹³C-labeled recovery standard was spiked for HRGC/HRMS (HP6890GC-Micromass Autospec Ultima) analysis. Tetra to octa-chlorinated PCDD/Fs and dioxin-like PCBs were quantified with DB-5 column (J&W Scientific)⁷.

Stable isotope analysis:

For carbon and nitrogen isotope ratio analysis, 1mg of freeze-dried samples were placed in a tin capsules. And carbon and nitrogen isotope ratios were determined by an isotope ratio mass spectrometer (Thermo Fisher Scientific Mat253) interfaced with an Elemental Analyzer (Thermo Fisher Scientific FlashEA1112).

Results and Discussion

Dioxin level and isotope ratio:

The concentration of dioxins and stable isotope ratios in earthworm, insect, plant, field mouse and bird are shown in **Table 1**. TEQ was highest in raptor species and followed by mouse liver, other birds, earthworm, plant and insect.

Table 1 The concentration of dioxins and stable isotope ratio

Species Congeners (pg/g-fat)	Northern goshawk A (Muscle)	Northern goshawk B (Muscle)	Brown-eared bulbul (Muscle)	Peregrine falcon (Muscle)	Scaly thrush (Muscle)	Japanese sparrow hawk (Muscle)	Insects Orthoptera (Whole body)	Philadelphia daisy (Leaf & stock)	Large Japanese field mouse (Liver)	Earthworm (Whole body)
2,3,7,8-F	41.7	96.7	14.0	534	8.67	296	3.4	33.5	41.5	97.7
1,2,3,7,8-F	33.1	80.3	<1	92.4	9.64	165	<1	1.05	22.2	59.5
2,3,4,7,8-F	61.0	153	31.2	489	62.0	1,810	<1	1.43	4,980	59.9
1,2,3,4,7,8-F	53.0	142	<1	350	42.7	404	1.04	1.35	4,734	48.2
1,2,3,6,7,8-F	626	21,100	5.61	2,920	52.7	16,300	1.09	2.10	3,175	101
1,2,3,7,8,9-F	11.7	62.7	<1	25.1	2.54	151	<1	<1	53.7	2.19
2,3,4,6,7,8-F	62.8	589	1.75	100	50.5	860	1.14	3.36	10,900	172
1,2,3,4,6,7,8-F	64.6	140	<1	30.8	33.3	239	6.93	6.57	5,920	394
1,2,3,4,7,8,9-F	<1	97.2	<1	40.7	3.87	129	1.76	2.02	658	15.7
OCDF	<1.5	28.1	<1.5	<1.5	4.55	<1.5	<1.5	3.82	600	238
2,3,7,8-D	48.8	75.7	5.09	86.4	13.8	405	1.88	1.84	11.0	52.1
1,2,3,7,8-D	175	396	15.2	514	37.8	1,640	<1	<1	73.2	295
1,2,3,4,7,8-D	32.3	174	<1	161	16.7	591	<1	0.94	287	26.7
1,2,3,6,7,8-D	151	425	<1	264	31.9	1,530	<1	2.83	169	256
1,2,3,7,8,9-D	22.2	39.1	<1	26.9	5.09	131	<1	2.02	57.5	53.6
1,2,3,4,6,7,8-D	25.5	76.5	<1	138	23.9	258	6.66	17.1	3,260	1,090
OCDD	142	883	<1	1,720	62.6	781	73.2	92.4	7,100	20,400
PCB #81	401	266	2.85	3,270	50.0	4,290	3.97	14.7	36.2	44.9
PCB #77	3,110	917	4.45	15,500	32.3	7,270	39.8	124	114	531
PCB #123	3,600	15,800	<1.5	29,000	783	61,700	8.51	23.4	54.2	116
PCB #118	150,000	1,020,000	<1.5	1,790,000	4,380	2,499,000	303	720	2,660	4,260
PCB #114	5,000	51,000	<1.5	57,300	597	73,600	10.5	56.9	73.8	90.0
PCB #105	43,900	131,000	<1.5	508,000	3,900	670,000	101	292	852	1,330
PCB #126	2,100	3,110	29.8	19,100	373	35,400	9.92	17.0	12,100	125
PCB #167	12,900	93,100	<1.5	102,000	995	227,000	16.4	6.69	699	503
PCB #156	19,300	268,000	<1.5	175,000	1,760	387,000	16.0	23.4	1,490	619
PCB #157	5,320	70,800	<1.5	36,800	789	96,600	4.20	8.17	640	137
PCB #169	1,820	6,440	3.40	12,100	349	40,100	3.21	<1.5	1,130	32.7
PCB #189	5,600	92,800	<1.5	30,200	763	132,000	3.06	3.84	794	88.1
Total PCDD/Fs+ dioxin-like PCBs	255,000	1,780,000	119	2,780,000	15,200	4,260,000	620	1,463	62,700	31,200
Total TEQ (pg-TEQ/g-fat)	1,120	5,640	66.7	7,530	225	15,200	9.4	47.3	7,100	602
Stable 15N isotope ratio (‰)	6.12	7.10	4.72	9.63	5.27	7.01	3.31	0.03	2.91	3.97
Stable 13C isotope ratio (‰)	-21.3	-21.6	-25.6	-22.7	-25.8	-23.3	-26.0	-29.7	-21.7	-17.5

Relationship between dioxin concentration and trophic level:

Figure 2 shows relationship between logarithm of PCDD/F congener concentration and stable isotope ratio ($\delta^{15}\text{N}$). It indicates that 2,3,7,8-TeCDD/F concentrations are elevated with trophic level, while OCDD/F concentrations are not.

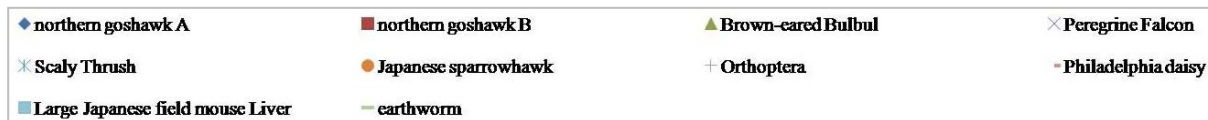
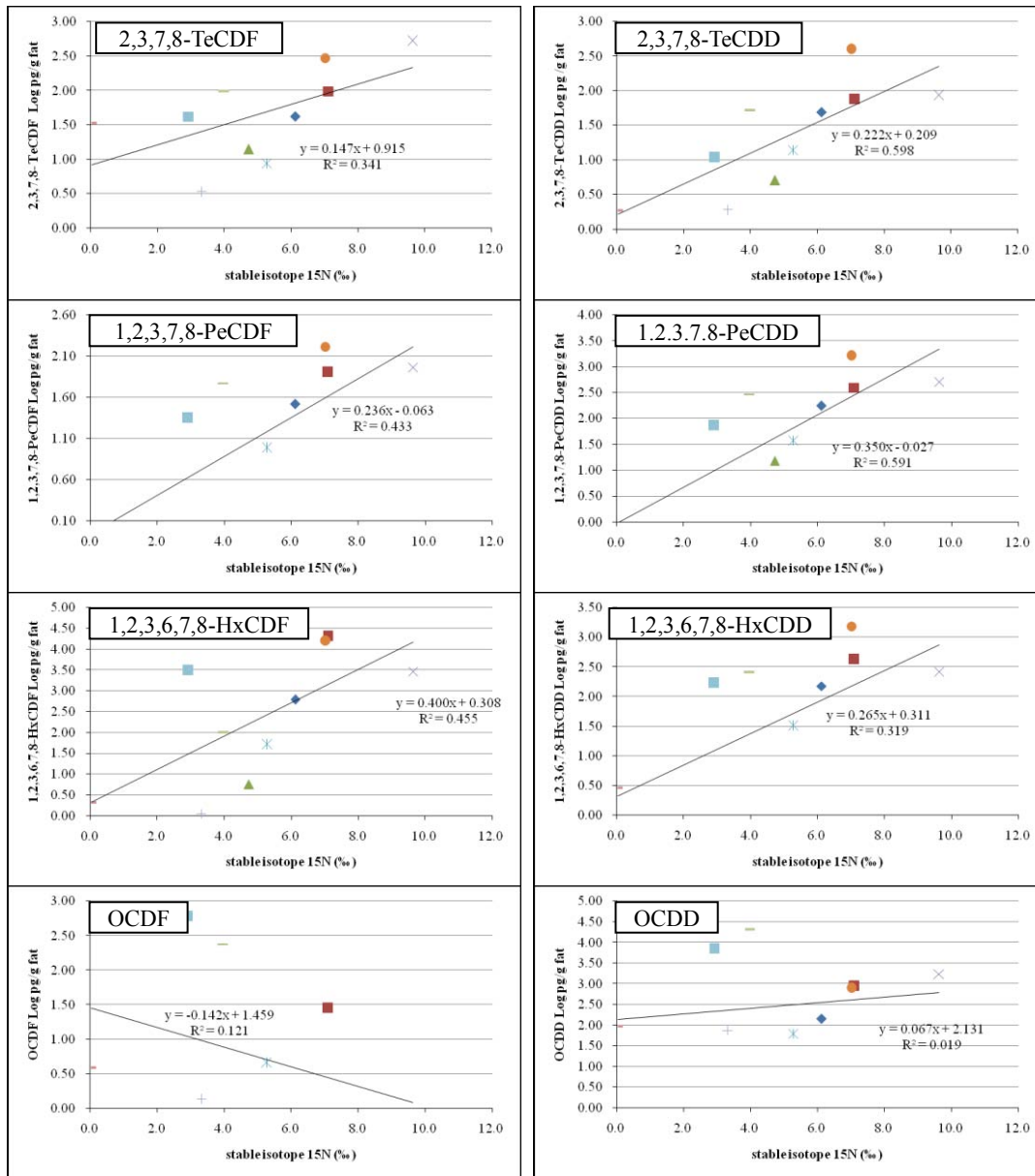


Figure 2 The concentration of PCDD/F congeners vs. stable nitrogen isotope ratio ($\delta^{15}\text{N}$) (PCDD/F concentrations are given in logarithmic scale)

The regression lines between logarithm of PCDD/F congener concentrations and $\delta^{15}\text{N}$ were calculated. **Table 2** shows their slopes, determination coefficients and P-values. Some lowly chlorinated (tetra- to penta-) PCDD/F congeners and most of dioxin-like-PCB congeners had significant linear regression relationship with $\delta^{15}\text{N}$. On the other hand, highly-chlorinated PCDD/Fs and some dioxin-like PCBs did not have significant linear correlation. The results indicated that lowly chlorinated dioxins and some dioxin-like PCBs are bioaccumulated through the terrestrial food chain although the samples in this study were collected from relatively wide area.

Table 2 Slopes, determination coefficients and P-values for regression equations between dioxin congener concentration and trophic level (stable nitrogen isotope ratio)

Congeners	Slope	R ²	P-value	Congeners	Slope	R ²	P-value
2,3,7,8-F	0.148	0.342	0.076	#81	0.311	0.571	0.012
1,2,3,7,8-F	0.238	0.431	0.039	#77	0.266	0.395	0.051
2,3,4,7,8-F	0.244	0.277	0.118	#123	0.460	0.554	0.014
1,2,3,4,7,8-F	0.214	0.199	0.196	#118	0.492	0.416	0.044
1,2,3,6,7,8-F	0.400	0.455	0.032	#114	0.467	0.522	0.018
1,2,3,7,8,9-F	0.218	0.372	0.061	#105	0.464	0.445	0.035
2,3,4,6,7,8-F	0.152	0.103	0.367	#126	0.336	0.464	0.030
1,2,3,4,6,7,8-F	0.039	0.009	0.797	#167	0.540	0.577	0.011
1,2,3,4,7,8,9-F	0.103	0.065	0.476	#156	0.529	0.521	0.018
OCDF	-0.142	0.121	0.324	#157	0.505	0.543	0.015
2,3,7,8-D	0.223	0.599	0.009	#169	0.500	0.577	0.011
1,2,3,7,8-D	0.350	0.592	0.009	#189	0.538	0.515	0.019
1,2,3,4,7,8-D	0.257	0.350	0.072				
1,2,3,6,7,8-D	0.265	0.320	0.088				
1,2,3,7,8,9-D	0.147	0.200	0.195				
1,2,3,4,6,7,8-D	0.041	0.010	0.787				
OCDD	0.068	0.020	0.700				

Conclusion

In this report, accumulation of dioxins in terrestrial trophic structure was discussed. Among PCDD/Fs, positive relation between logarithm of concentration in samples which range from earthworm to Northern Goshawk and trophic level based on stable isotope ^{15}N ratio were shown for tetra- to hexa-chlorinated PCDD/F congeners. The slope of linear regression equation for these congeners ranged from 0.15 to 0.53.

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