MONITORING OF PCB AND PCN DISTRIBUTION IN JAPAN USING PASSIVE AIR SAMPLERS

Masunaga S [1], Habib A [1, 2], Seike N [3], Kobara Y [3], Otani T [3]

[1] Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan
[2] University of Dhaka, Ramna, Dhaka, 1000, Bangladesh
[3] National Institute for Agro-Environmental Sciences, Tsukuba, 305-8604, Japan

Abstract
Polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) in air were measured using passive air sampler (PAS) across Japan as a part of broader monitoring program over East Asia. PAS with polyurethane foam (PUF) disk was exposed to air for eight weeks from March 21 to May 16, 2008 at 55 sites. The amounts of total PCB and PCN collected differed two orders of magnitude among sites and 7.9 – 1,400 and 0.43 – 32 ng/sample, respectively. The corresponding concentrations were estimated to be 81 – 14,000 and 7.8 – 570 pg/m^3, respectively. PCB concentrations were higher than PCN at all sites. The concentrations of PCB and PCN were generally higher at urban sites than rural sites. Homologue profiles of PCB and PCN showed that lower chlorinated homologues (di- and tri-chlorinated for PCB and tri- and tetra-chlorinated for PCN) were more abundant than higher chlorinated ones at most sites. However, some sites had quite different homologue profiles. The PCB congener profiles at all sites were similar to that of Kanechlor indicating PCB formulations were the major source. On the other hand, the PCN congener profiles had some variation among sites and were generally different from that of Halowax formulation.

Introduction
Although the production and new use of polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs) have been prohibited worldwide, they continue to be detected in the atmosphere as a result of emissions from remaining usage, contaminated environmental surfaces such as soil and unintentional formation such as combustion. PCBs and PCNs were manufactured commercially as technical mixtures with different trade names and PCNs also occur as impurities in PCB formulations. They are well known persistent organic pollutants (POPs) due to their toxicity, bioaccumulation, and resistance to environmental degradation. In this study, monitoring of PCBs and PCNs has been carried out using passive air samplers (PASs) to grasp the distribution of these compounds in air. The use of the samplers made it possible to conduct monitoring of many sites at the same time [1 - 5]. The obtained results are expected to provide useful information to identify the current emission sources of those chemicals to air. This study will be a part of the regional scale monitoring program in East Asia with the cooperation of Guangzhou Institute of Geochemistry, China, National Institute of Agricultural Science and Technology, Korea and University of Dhaka, Bangladesh.

Materials and Methods
Sampling with passive air samplers (PASs): The PAS with polyurethane foam (PUF) disk (φ140 × 13 mm) used in this study have been described previously [1, 4]. PUF disks were pre-cleaned by extraction. PASs were assembled with cleaned PUF disks and transported to the deployment sites sealed in polyethylene bags. The samplers were deployed for 56 days (8 weeks) from March 21, 2008 to May 16, 2008 at 55 sites. Sampling locations are shown in **Table 1**. Among the 55 sites, 37 were rural, 4 were suburban and 14 were urban sites across Japan. Rural sampling sites were chosen on the condition that they were distant from any known local sources or significant human activity. At the end of the deployment period, the PASs were retrieved, resealed in poly-bags and returned to the laboratory. On receipt, the PUF disks were taken out and stored in a freezer until extraction. Along with three passive samplings, an active sampling (100 L/min) was carried out by weekly changing PUFs and quartz fiber filters at one site (Tsukuba, Ibaraki).

Pretreatment and analysis: In the laboratory, the PUF disks were Soxhlet extracted with acetone and spiked with a range of $^{13}C_{12}$-labeled PCBs congeners to ensure the cleanup procedures. The pretreatment procedure is shown roughly in **Figure 1**. Then, the extracts were reduced to a final volume of 100 μl under a gentle stream

of nitrogen and solvent was changed to 100 µl of decane containing internal standards. The samples were analyzed for PCBs and PCNs on a HRGC-HRMS operated in electron ionization mode using selected ion monitoring (SIM). A total of 129 PCB congeners (di- to octa-chlorinated) and 47 PCN congeners (tri- to octa-chlorinated) were quantified.

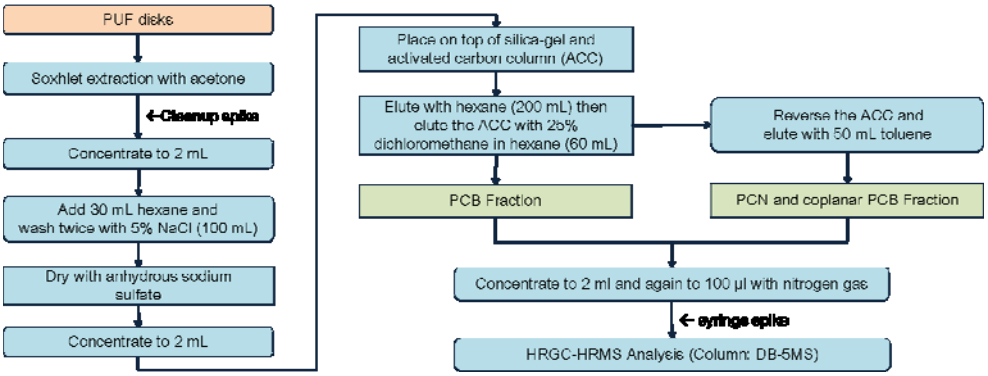

Figure 1 Pretreatment and analysis procedure

Results and Discussion

Sampling rates: Sampling rates were calculated by comparing the results of concurrent active [gas phase only] (n=1) and passive (n=3) samplings. Both samplings were carried out in Tsukuba and the passive results (Site numbers 56, 57, 58) were averaged. The results were analyzed from two perspectives: (i) by comparison of the total amount of each homologue and (ii) by the slope of regression line among isomers. For penta- to hepta-chlorinated PCB homologues, the regressions were not good enough to estimate reliable sampling rates, probably due to the low amounts of PCBs collected by the two methods. For hepta- and octa-chlorinated PCNs, the second estimation method was not possible as their numbers of isomers were less than two. The obtained results are shown in **Table 1**. The estimated sampling rate was highest for dichlorobiphenyl and decreased as the degree of chlorination increased. Then, the rate was lowest for tetrachlorobiphenyl and again increased as the degree of chlorination. Similar results were obtained for PCNs. In this case, lowest sampling rate was observed for tetrachloronaphthalene.

Table 1 Sampling rates estimated by concurrent active and passive samplings

Method of Estimation / Homologues	Sampling rate (m^3/day)		Method of Estimation / Homologues	Sampling rate (m^3/day)	
	Total of isomers	Slope of regression line [Rate and (R^2)]*		Total of isomers	Slope of regression line [Rate and (R^2)]
Dichlorobiphenyl	4.48	5.01 (0.95)	-		
Trichlorobiphenyl	1.42	1.31 (0.90)	Trichloro naphthalene	1.14	1.10 (0.82)
Tetrachlorobiphenyl	0.878	0.84 (0.81)	Tetrachloronaphthalene	0.777	0.81 (0.97)
Pentachlorobiphenyl	1.30	*0.41 (0.48)*	Pentachloronaphthalene	1.11	0.97 (0.53)
Hexachlorobiphenyl	1.78	*0.85 (0.21)*	Hexachloronaphthalene	2.46	*1.67 (0.15)*
Heptachlorobiphenyl	2.41	*1.82 (0.04)*	Heptachloronaphthalene	3.66	- (-)
Octachlorobiphenyl	2.85	2.75 (0.74)	Octachloronaphthalene	7.66	- (-)
Total PCBs	1.76	- (-)	Total PCNs	0.985	- (-)

* Values in italic fonts indicate that their reliability was low.

PCB and PCN concentrations: Amounts of PCB and PCN collected by PUF disks (pg/sample) and their corresponding concentrations in air are shown in **Table 2** and graphically in **Figures 2 and 3**. The concentrations in air were estimated assuming the sampling rate for PCB and PCN to be 1.76 and 0.982 m^3/day, respectively. The results indicated that higher amounts were observed for PCBs (range: 7,900 - 1,400,000 pg/sample) than for PCNs (range: 430 - 32,000 pg/sample) at all sites. Moreover, higher concentrations of PCBs and PCNs were generally observed for the samples at urban sites in Kanto Region and around the Seto Inland Sea compared to the rural sites. Exceptionally high concentrations of PCBs and PCNs, however, were observed at Kushimoto, Wakayama (Site 25) which is a rural site. At this moment, we are not yet sure of why

quite high concentrations were observed at certain sites. As current results are from one time sampling only, we will confirm whether these situations are common in the future rounds of samplings.

Relationship between PCB and PCN concentrations: The concentrations of total PCBs and PCNs had positive correlation, which indicated that they have common sources (**Figure 4**). However, the correlation became much weaker when the highest site (Site 25) was removed. Relatively clear correlation was observed for urban sites while the correlation among rural sites was much weaker.

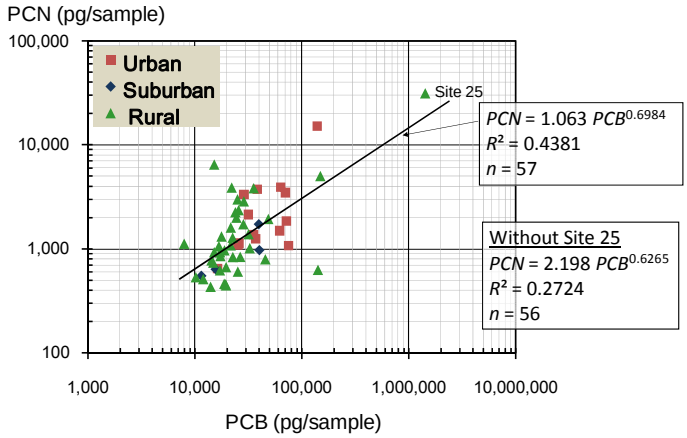

Figure 4 Relationship of total PCB and PCN collected by PAS

Homologue profiles: PCB and PCN homologue profiles showed that lowly chlorinated homologues (di- and tri-chlorinated for PCB and tri- and tetra-chlorinated for PCN) were more abundant than highly chlorinated homologues at most sites (**Figures 5 and 6**). However, there were some sites (Sites 14 [Bunkyo, Tokyo], 28 [Takasago], 38 [Matsuyama] and 40 [Uwajima]) where tetra- to hexa-chlorinated PCB homologues were as abundant as less chlorinated ones. Peculiar PCN homologue profiles were observed at Sites 13 [Nasu], 17 [Ogasawara], 25 [Kushimoto], 46 [Isahaya] and 52 [Makurazaki].

Congener profiles: The PCB congener profiles in each homologue were generally similar to those of Kanechlor formulations. This indicated that Kanechlors were the major source of PCB in atmosphere all over Japan. On the other hand, the PCN congener profiles had some variation among sites and the profiles were different from that of Halowax formulations. Although the concentrations of CPN in air were quite low and their profiles were not so reliable, the present results indicated the existence of some other sources of PCN.

We measured the concentrations of PCB and PCN all over Japan. These were from only one time sampling. Thus, we are planning to repeat this type of sampling and will confirm the results obtained in this study.

Acknowledgements
The authors would like to thank the many people across Japan who helped us to set and retrieve the passive air samplers. This study was supported in part by the Global COE Program "Eco-risk Asia" of the Ministry of Education, Culture, Sports, Science and Technology of Japan and by the FY 2008 Cooperative research project of the Graduate School of Environment and Information Sciences, Yokohama National University.

References
1. Shoeib, M. and Harner, T. *Environ Sci Technol* 2002, 36:4142-4151.
3. Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., and Jones, K.C. *Environ Sci Technol* 2004, 38:34-41.
2. Harner, T., Shoeib, M., Diamond, M., Stern, G., and Rosenberg, B. *Environ Sci Technol* 2004, 38:4474-4483.
4. Jaward, F. M., Farrar, N. J., Harner, T., Sweetman, A. J., and Jones, K. C. *Environ Toxicol Chem* 2004, 23:1355-1364.
5. Jaward, F. M., Zhang, G., Nam, J. J, Sweetman, A. J., Obbard, J. P., Kobara, Y., and Jones, K. C., *Environ Sci Technol* 2005, 39:8638-8645.

Table 2 Total PCB and PCN collected by PAS and their estimated concentration in air*

ID	Location of sampling site	Latitude	Longitude	Type	Total PCB (pg/sample)	Total PCB** (pg/m^3)	Total PCN (pg/sample)	Total PCN** (pg/m^3)
1	Hamatonbetsu, Hokkaido	45:06:35	142:21:47	Rural	14,000	140	430	7.8
2	Nakashibetu, Hokkaido	43:32:20	144:59:44	Rural	20,000	200	450	8.1
3	Naganuma, Hokkaido	43:03:08	141:45:39	Rural	17,000	180	930	17
4	Sapporo, Hokkaido	42:59:25	141:24:15	Suburban	40,000	410	970	18
5	Kuroishi, Aomori	40:38:44	140:35:08	Rural	46,000	460	800	14
6	Yamagata, Yamagata	38:14:53	140:14:53	Rural	14,000	150	780	14
7	Kitakami, Iwate	39:21:08	141:06:18	Rural	140,000	1,400	630	11
8	Koriyama, Fukushima	37:28:23	140:23:45	Rural	23,000	230	1,300	23
9	Suzu, Ishikawa	37:26:11	137:16:17	Rural	19,000	200	460	8.3
10	Komatsu, Ishikawa	36:24:08	136:27:53	Urban	37,000	380	1,300	23
11	Seiro, Niigata	37:59:07	139:17:58	Rural	20,000	200	670	12
12	Sado, Niigata	38:00:50	138:21:32	Rural	19,000	190	460	8.4
13	Nasushiobara, Tochigi	36:55:02	139:56:08	Rural	15,000	150	6,500	120
56	Tsukuba, Ibaraki	36:01:11	140:07:17	Rural	35,000	360	3,800	70
57					26,000	260	2,400	43
58					24,000	250	2,000	36
14	Bunkyo-ku, Tokyo	35:42:05	139:45:41	Urban	140,000	1,400	15,000	270
15	Tachikawa, Tokyo	35:41:39	139:23:45	Urban	29,000	290	3,300	61
16	Hachijo, Tokyo	33:06:59	139:47:00	Rural	18,000	180	1,300	24
17	Ogasawara, Tokyo	27:03:55	142:12:22	Rural	7,900	81	1,100	20
18	Hodogaya, Yokohama, Kanagawa	35:28:12	139:35:34	Urban	38,000	390	3,800	68
19	Tateyama, Chiba	34:58:59	139:54:12	Rural	19,000	190	970	18
20	Suzaka, Nagano	36:39:36	138:18:51	Rural	25,000	250	3,000	55
21	Okitsu, Shimizu, Shizuoka	35:03:05	138:31:32	Rural	32,000	320	1,400	25
22	Nagakute, Aichi	35:09:38	137:04:23	Suburban	16,000	160	640	12
23	Matamaru, Gifu, Gifu	35:26:18	136:42:11	Urban	62,000	630	1,500	27
24	Kashihara, Nara	34:29:46	135:47:17	Rural	28,000	290	1,700	31
25	Kushimoto, Wakayama	33:28:27	135:47:23	Rural	1,400,000	14,000	32,000	570
26	Izumi, Osaka	34:26:24	135:26:50	Suburban	40,000	410	1,700	31
27	Suma, Kobe, Hyogo	34:38:45	135:08:05	Urban	64,000	650	3,900	71
28	Takasago, Hyogo	34:45:47	134:47:36	Urban	72,000	730	1,900	34
29	Nishiwaki, Hyogo	34:59:27	134:58:23	Urban	25,000	260	1,100	20
30	Toyooka, Hyogo	35:22:51	134:49:28	Rural	25,000	260	610	11
31	Takarazuka, Hyogo	34:48:15	135:21:31	Urban	26,000	260	1,100	21
32	Tottori, Tottori	35:30:39	134:10:37	Suburban	12,000	120	550	10
33	Izumo, Shimane	35:19:41	132:43:58	Rural	22,000	220	1,100	20
34	Okinoshima, Shimane	36:11:58	133:19:50	Rural	33,000	330	1,000	19
35	Higashihiroshima, Hiroshima	34:25:01	132:41:54	Rural	10,000	100	540	9.7
36	Setoda, Hiroshima	34:18:08	133:05:26	Rural	150,000	1,500	5,000	91
37	Bunkyo, Matsuyama, Ehime	33:50:05	132:45:23	Urban	36,000	360	1,400	25
38	Sanban-cho, Matsuyama, Ehime	33:50:05	132:45:23	Urban	70,000	710	3,500	63
39	Niihama, Ehime	33:55:50	133:10:59	Urban	32,000	320	2,100	39
40	Uwajima, Ehime	33:13:27	132:34:23	Urban	75,000	760	1,100	20
41	Tengkogen, Ehime	33:28:26	133:00:24	Rural	17,000	170	620	11
42	Nankoku, Kochi	33:35:19	133:38:52	Rural	15,000	150	930	17
43	Chikushino, Fukuoka	33:30:22	130:34:22	Rural	22,000	220	1,600	29
44	Yukuhashi, Fukuoka	33:42:35	130:58:45	Rural	22,000	220	3,900	71
45	Ookimachi, Fukuoka	33:12:16	130:26:07	Rural	29,000	290	2,900	52
46	Isahaya, Nagasaki	32:49:52	130:01:36	Rural	27,000	270	840	15
47	Shinkamigoto, Nagasaki	32:59:16	129:04:16	Rural	17,000	170	1,100	19
48	Sadoharai, Miyazaki	32:00:01	131:27:56	Rural	23,000	230	840	15
49	Usa, Oita	33:31:57	131:23:20	Rural	24,000	240	2,300	41
50	Goshi, Kumamoto	32:53:07	130:45:55	Rural	49,000	490	2,000	35
51	Minamisatsuma, Kagoshima	31:28:43	130:20:39	Rural	17,000	180	850	16
52	Makurazaki, Kagoshima	31:15:59	130:21:01	Rural	15,000	150	740	13
53	Naha, Okinawa	26:12:14	127:43:23	Urban	16,000	170	650	12
55	Ishigaki, Okinawa	24:22:22	124:11:40	Rural	12,000	120	510	9.3

* Total PCB = Total of di- to octa-chlorinated PCB congeners; Total PCN = Total of tri- to octa-chlorinated PCN congeners.
** Concentrations were estimated by assuming sampling rate for PCB and PCN to be 1.76 and 0.985 m^3/day, respectively.

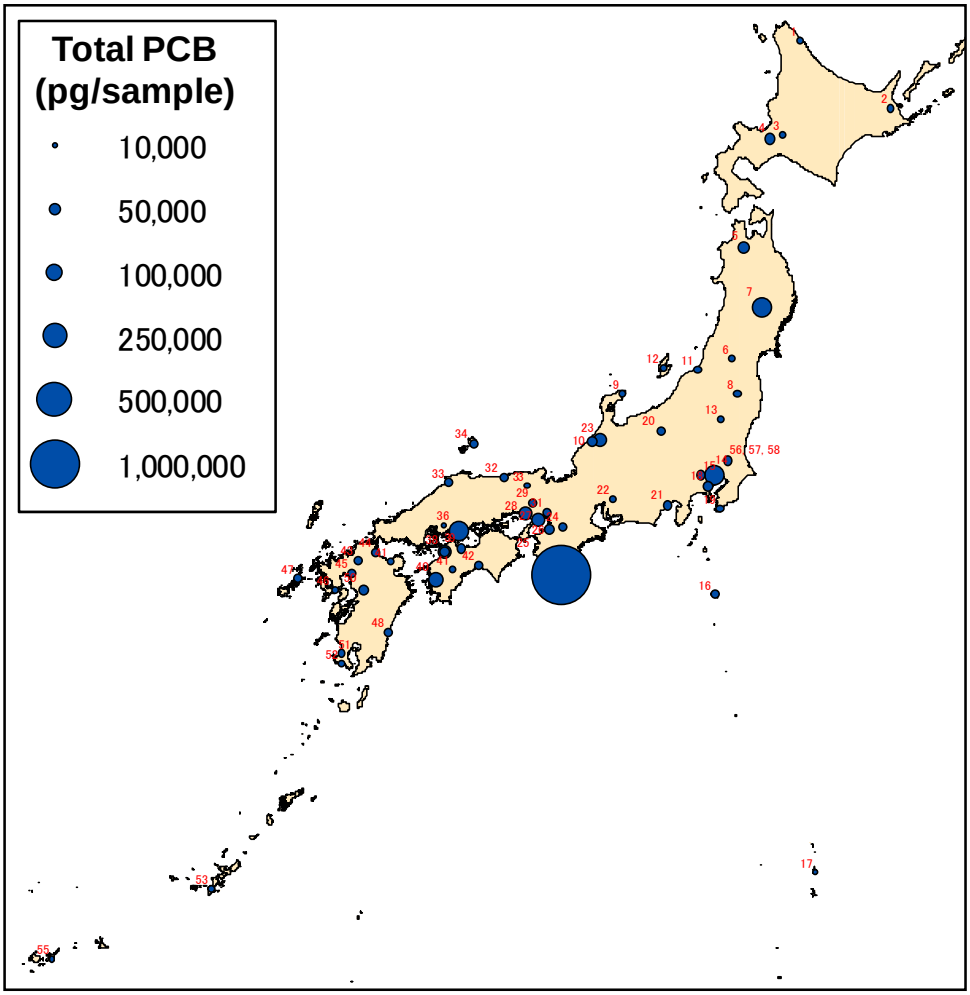

Figure 2 Amount of PCBs collected by PAS at each sampling site

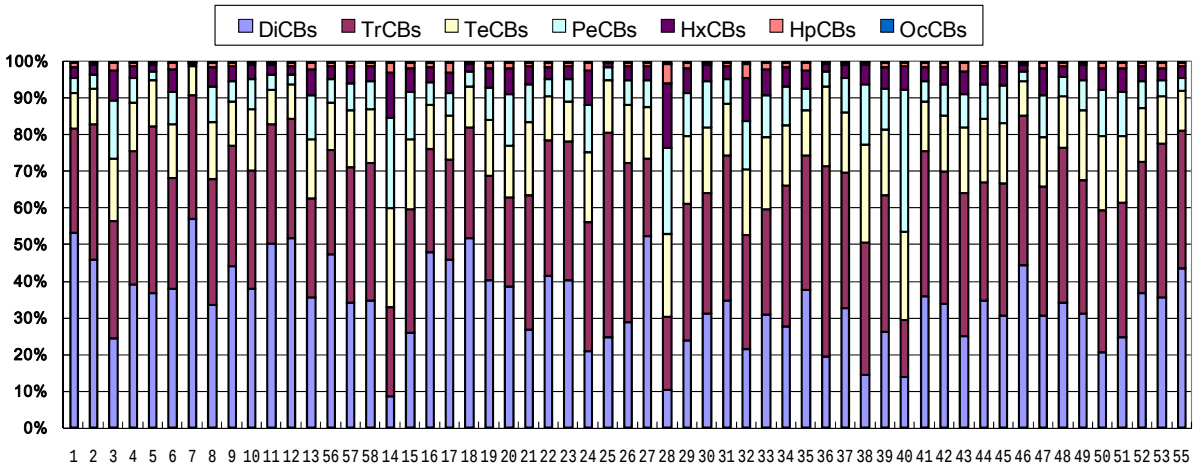

Figure 5 PCB homologue profile at each sampling site

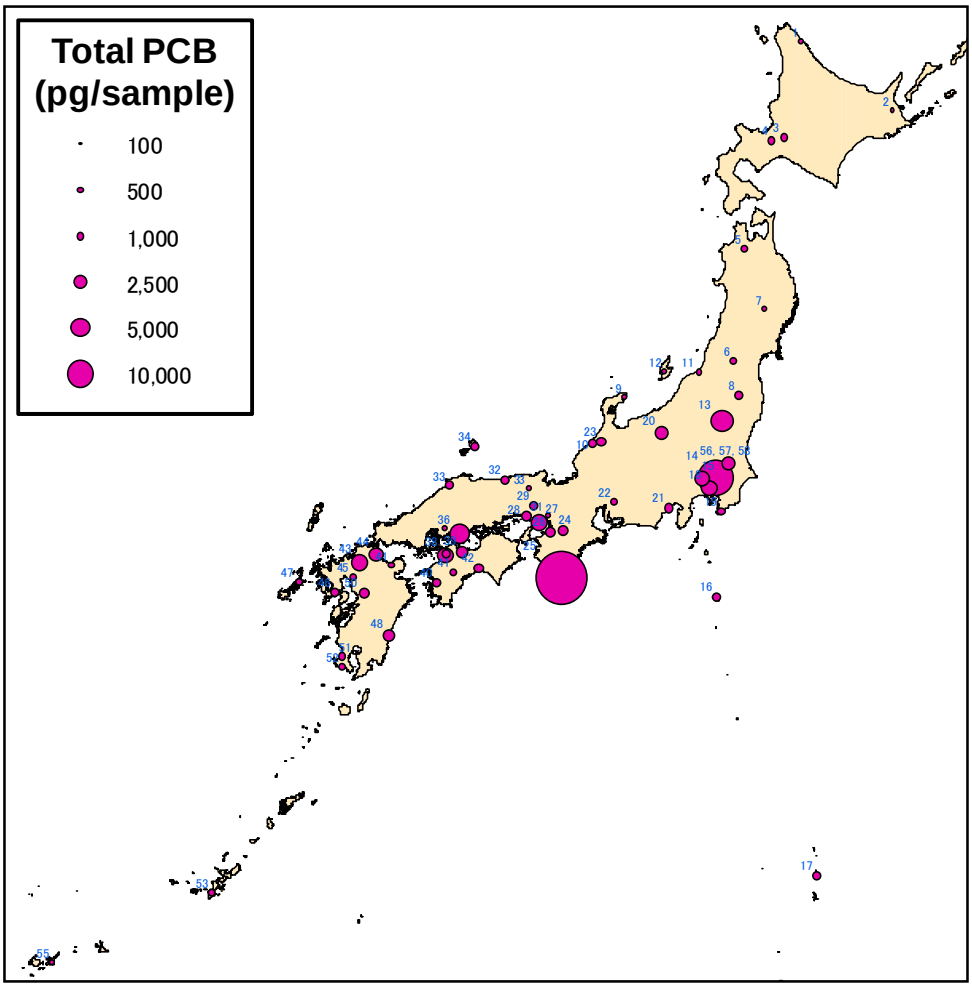

Figure 3 Amount of PCNs collected by PAS at each sampling site

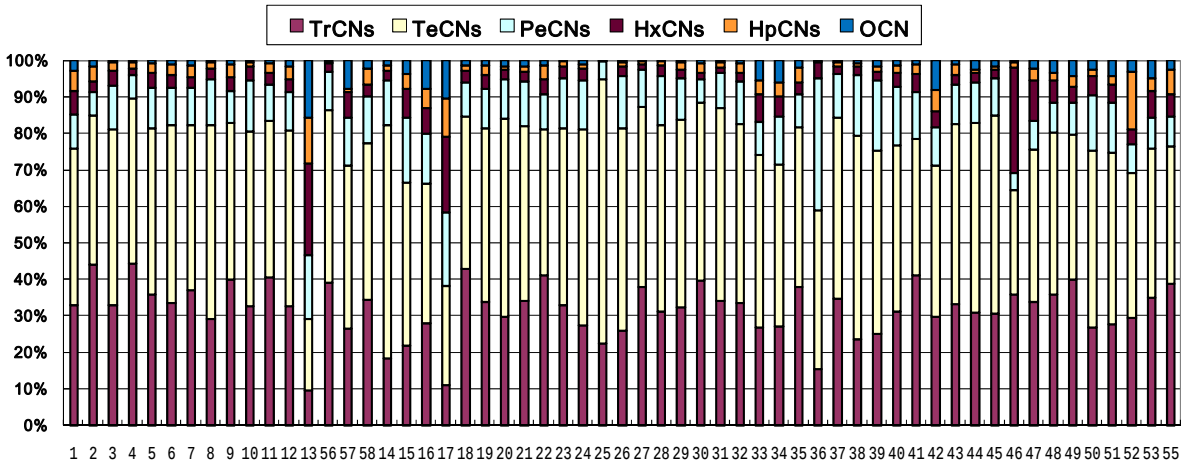

Figure 6 PCN homologue profile at each sampling site