PRELIMINARY RESULTS OF ATMOSPHERIC POLYCHLORINATED DIBENZO-*p*-DIOXIN/FURAN/BIPHENYL AND POLYBROMINATED DIPHENYL ETHER CONCENTRATIONS IN THE PACIFIC OCEAN NEAR SOUTHERN TAIWAN AND PHILIPPINES

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Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans(PCDFs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are ubiquitous in environment which mainly arise from industrial sources or combustion. They are a class of persistent organic pollutants (POPs) with resistance to chemical, physical, and biological degradation, lipophilicity, bioaccumulation, and biomagnifications. PCDD/Fs, PCBs, and PBDEs have caused the potential adverse effect on ecosystem and human. Due to the characteristic of bioaccumulation, these organohalogens can accumulate in food chain and foodstuffs[1]. Fish and seafood have been reported as one of important sources for human exposure to POPs for an example of PCBs[2]. Several *in-vivo* and *in-vitro* studies have shown that POPs are associated with reproductive dysfunction, immunotoxicity, neurobehavioral disorders, and disruption of hormones. For the environmental epidemiological studies, our previous studies have been demonstrated that PCDD/Fs, PCBs, and PBDEs had possibly induced the smaller birth outcomes, the delay of menstrual cycle, disruption of thyroid hormones, growth hormones and steroid sex hormones, and children's neurodevelopment[3-10]. Therefore, these organohalogen compounds have been raised the globally public concern.

The atmosphere is the major pathway for transportation of POPs. The long-range atmospheric transport (LRAT) is a rapid route of transporting POP chemicals to the other locations[11,12]. Chi et al. (2010) revealed that atmospheric PCDD/F levels were significantly increased at a high-altitude background station in central Taiwan in the duration of the southeast Asia biomass burning event probably due to LRAT of PCDD/Fs from southeast Asian countries[13]. Chi et al. (2013) was evaluated the deposition flux of PCDD/Fs in high-mountain air sample in central Taiwan, indicating PCDD/Fs ranged from 0.61-3.0 pg I-TEQ/m^2/day and 0.49 ± 0.03 ng I-TEQ/m^2/year significant lower than other Asian countries[14]. Several studies investigated atmospheric PCBs in the ocean such as in East and South China Seas(77 pg/m^3) and in South Atlantic Ocean(20 pg/m^3)[15]. Only a few reports were focused on levels of PCDD/Fs and PBDEs in the marine atmosphere particularly for the ambient air on the ocean[16-19]. Although background atmospheric levels of PCDD/Fs, PCBs, and PBDEs in the ocean are recognized in the most scientists due to extremely lower levels in the ambient air on the ocean compared to those on the terrestrial land, ocean is a natural cumulative reservoir for POPs contaminants associated with aquatic organism exposure to POPs and global burden of POPs. This study was the first one to investigate atmospheric levels of PCDD/Fs, PCBs, and PBDEs in the Pacific Ocean near Southern Taiwan and Philippines.

Materials and methods

Atmospheric samples on the ocean were taken by two high-volumn air samplers installed on the deck in the R/V Ocean Researcher V (OR5), which is a research vessel from the Taiwan Ocean Research Institute, National Applied Research Laboratories(TORL/NARL) between November 1 to November 6 in 2012. The atmospheric air samples were collected in the three routes including A, B, and C, which are on the ocean near southern Taiwan and Pillipines (Figure 1) . Each air sample was collected approximately 40 h (1-2 days, ~600 m^3) with a PS-1 sampler (Graseby Andersen, GA) following US EPA Reference Method TO9A. A quartz fiber filter followed by PUF captured particle and gas phase. After the collection, the quartz fiber filter and PUF of each air sample were combined to be analyzed for PCDD/Fs, PCBs, and PBDEs. Concentrations are reported with

respect to standard conditions of 760 mm Hg and 298 K and denoted as Nm^3.

In this study, the fourteen PBDEs (BDE-28, 47, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 208 and 209), twelve PCBs (PCB-77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 and 189) and seventeen 2,3,7,8-substituted PCDD/F congeners were investigated. Analyses of PBDEs, PCBs and PCDD/Fs were performed following US EPA Method 1614 and Method M1668A. The internal standards of PBDEs, PCBs and PCDD/Fs were spiked to the samples before Soxhlet extraction with toluene, and were used to monitor the extraction and cleanup procedures. The detailed analytical procedures for PBDEs and PCDD/Fs are given in our previous studies[20,21]. After sample pretreatment process, the extracted solution was divided into two equal aliquots. One aliquot was used to measure PBDEs, PCBs and PCDD/Fs, while the other was stored for possible use. The final elute was analyzed by a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) (Hewlett-packard 6970 Series GC/Micromass Autospec Ultima) equipped with a DB-5HT capillary column (L=60, i.d.=0.25 mm, film thickness= 0.1 μm)(J&W Scientific, CA).The HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The analyzer mode of the selected ion monitoring (SIM) was used with a resolving power of 10000. The detailed instrumental analysis parameters of PBDEs and PCDD/Fs are given in our previous studies[20,22]. The quality assurance and quality control (QA/QC) in this study was met to the criteria of US EPA Method 1614 and M1668A.

Results and discussion

The total (summation of gaseous and particulate phases) PCDD/Fs concentration of three atmospheric samples were listed in Table 1. The Σ_{14} PCDD/Fs range of three atmospheric samples were 10.8×10^{-4} to 108×10^{-4} pg I-TEQ/Nm^3, and the mean and standard deviations of Σ_{14} PCDD/Fs was $49.4\times10^{-4} \pm 51.57\times10^{-4}$ pg I-TEQ/Nm^3. The dominant TEQ congener of PCDD/Fs were 2,3,4,7,8-PeCDF and 1,2,3,4,7,8-HxCDF, their were contribution approximately 37% and 10% of the atmospheric samples in this study. This is the first data to show PCDD/F measurements in marine atmosphere near Taiwan. However, our values (mean: 49.43×10^{-4} pg I-TEQ/Nm^3) were dramatically lower than the Heavy steel complex area(mean: 0.135 pg I-TEQ/Nm^3) , Metals complex areas (0.082 pg I-TEQ/Nm^3) and Urban areas (mean: 0.0281 pg I-TEQ/Nm^3)[23] in Taiwan.

In the Table 2, Σ_{12} PCBs concentrations of atmospheric samples on three site in Pacific Ocean were ranged from 0.21 to 0.47 pg/Nm^3, while the mean of Σ_{12} PCBs was 0.32 pg/Nm^3. PCB-118 was the highest concentration among 12 PCB congeners and the measurements of PCB-167 was lower than limits of detection (LODs) in each atmospheric sample. Compared with the results in the land-based studies[24,25], PCBs distribution and PCB levels were different from our PCB data in the atmospheric ocean. Baek et al., (2011) monitored of PCBs congeners distribution in polar regions since 2005 to 2009, their results showed the predominant PCB congener was DiCB[24]; Melymuk et al., (2012) investigated PCBs concentration in Toronto air , the concentration of ΣPCBs ranged from 6.0 to 1300 pg/ m^3 extremely higher than our results[25]. Compared with the recent oceans study, our values (mean of Σ_{12} PCBs: 0.32 pg/Nm^3) were 62.5- 240.6 times lower than East and South China Seas (mean of Σ_7 PCBs: 77 pg/m^3), Andaman Sea and Bay of Bengal (mean of Σ_7 PCBs: 30 pg/m^3), Indian Ocean (mean of Σ_7 PCBs: 42 pg/m^3), North Atlantic Ocean (mean of Σ_7 PCBs: 23 pg/m^3) and South Atlantic Ocean (mean of Σ_7 PCBs: 20 pg/m^3)[15]. The low PCB levels in the present study was probably due to short duration sampling in the Northeast monsoon.

In the Table 3, Σ_{14} PBDEs concentrations ranged from 15.92 to 23.54 pg/Nm^3 with a mean of 21.62 pg/Nm^3. All of the PBDEs congeners were higher than LODs. The dominant congener among 14 PBDE congeners was BDE-209, consisting 84% of ΣPBDEs in atmospheric samples in Pacific Ocean. This result showed a similar trend of PBDEs congeners distribution with almost atmospheric studies. Möller et al., (2012) and Xie et al., (2011) were observed ΣPBDEs without BDE-209 concentration of 0.78 and 0.13 pg/m^3, respectively, in Southern Ocean[17,18]. Compared with the previous two studies from Southern Ocean[17,18], our values without BDE-209 (mean: 3.53 pg/Nm^3) were higher approximately 4.53-27.2 times higher. Our results are only lower than those reported in the East Asian Seas of the Pacific Ocean[26] as well as the East and South China Seas of the Pacific Ocean [27] and comparable to those in the East Indian Archipelago and Philippine Sea of the Pacific Ocean[18].

In conclusion, atmospheric PBDE concentrations in three routes on Pacific Ocean near Southern Taiwan and Philippines were no high compared to the previous reports. However, atmospheric PCBs concentrations in the present study were the lowest among the recent PCB data in the ocean atmospheric studies. Future work will focus on LRAT of POP chemicals including PCDD/Fs, PCBs, PBDEs, PBBs, PCDEs, and PBDD/Fs in the atmosphere in South China Sea or Pacific Ocean near western Taiwan.

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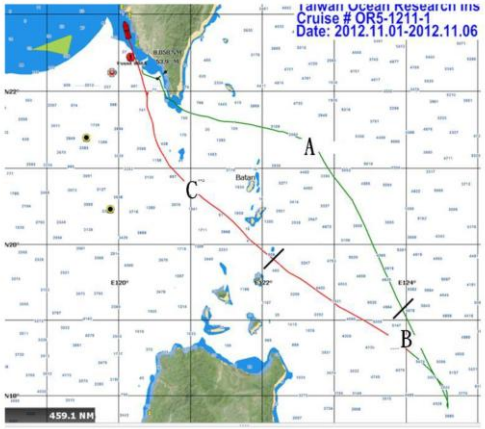

Figure 1. The location of three atmospheric samples in Southern Ocean

Table 1. Level of PCDD/Fs of three atmospheric samples in Southern Ocean

	Mean(pg I-TEQ/Nm^3)	SD	Range(pg I-TEQ/Nm^3)
2,3,7,8-TeCDF	3.14×10^{-4}	2.70×10^{-4}	$0.94 \times 10^{-4} \sim 6.17 \times 10^{-4}$
1,2,3,7,8-PeCDF	1.97×10^{-4}	1.84×10^{-4}	$0.49 \times 10^{-4} \sim 4.03 \times 10^{-4}$
2,3,4,7,8-PeCDF	18.47×10^{-4}	21.86×10^{-4}	$0.37 \times 10^{-7} \sim 42.60 \times 10^{-4}$
1,2,3,4,7,8-HxCDF	5.27×10^{-4}	5.75×10^{-4}	$0.99 \times 10^{-4} \sim 11.80 \times 10^{-4}$
1,2,3,6,7,8-HxCDF	4.75×10^{-4}	5.24×10^{-4}	$0.81 \times 10^{-4} \sim 10.7 \times 10^{-4}$
2,3,4,6,7,8-HxCDF	3.94×10^{-4}	4.13×10^{-4}	$0.77 \times 10^{-4} \sim 8.62 \times 10^{-4}$
1,2,3,7,8,9-HxCDF	0.44×10^{-4}	0.44×10^{-4}	$< 0.12 \times 10^{-4} \sim 0.25 \times 10^{-4}$
1,2,3,4,6,7,8-HpCDF	1.52×10^{-4}	1.67×10^{-4}	$0.29 \times 10^{-4} \sim 3.42 \times 10^{-4}$
1,2,3,4,7,8,9-HpCDF	0.20×10^{-4}	0.24×10^{-4}	$< 0.39 \times 10^{-5} \sim 0.48 \times 10^{-4}$
OCDF	0.15×10^{-4}	0.15×10^{-4}	$0.32 \times 10^{-5} \sim 0.32 \times 10^{-4}$
2,3,7,8-TeCDD	3.42×10^{-4}	1.84×10^{-4}	$< 2.09 \times 10^{-4} \sim 5.52 \times 10^{-4}$
1,2,3,7,8-PeCDD	2.82×10^{-4}	1.85×10^{-4}	$1.61 \times 10^{-4} \sim 4.95 \times 10^{-4}$
1,2,3,4,7,8-HxCDD	1.30×10^{-4}	1.08×10^{-4}	$< 0.20 \times 10^{-4} \sim 1.31 \times 10^{-4}$
1,2,3,6,7,8-HxCDD	1.03×10^{-4}	1.09×10^{-4}	$0.34 \times 10^{-4} \sim 2.29 \times 10^{-4}$
1,2,3,7,8,9-HxCDD	1.17×10^{-4}	1.10×10^{-4}	$0.44 \times 10^{-4} \sim 2.44 \times 10^{-4}$
1,2,3,4,6,7,8-HpCDD	0.77×10^{-4}	0.91×10^{-4}	$0.15 \times 10^{-4} \sim 1.82 \times 10^{-4}$
OCDD	0.32×10^{-4}	0.21×10^{-4}	$0.14 \times 10^{-4} \sim 0.55 \times 10^{-4}$
Σ_{14} PCDD/Fs	49.43×10^{-4}	51.57×10^{-4}	$10.8 \times 10^{-4} \sim 108 \times 10^{-4}$

Table 2. Level of PCBs of three atmospheric samples in Southern Ocean

	Mean(pg/Nm^3)	SD	Range(pg/Nm^3)
PCB#77(4CL)	0.042	0.0077	0.036 ~ 0.050
PCB#81(4CL)	0.0039	0.0017	0.0023 ~ 0.0056
PCB#105(5CL)	0.068	0.027	0.045 ~ 0.098
PCB#114(5CL)	0.0089	0.0062	0.0036 ~ 0.016
PCB#118(5CL)	0.17	0.076	0.11 ~ 0.26
PCB#123(5CL)	0.0056	0.0036	0.0033 ~ 0.0098
PCB#126(5CL)	0.0041	0.0020	0.00256 ~ 0.0064
PCB#156(6CL)	0.011	0.0056	0.0073 ~ 0.018
PCB#157(6CL)	0.0029	0.0014	0.0017 ~ 0.0045
PCB#167(6CL)	< 0.0073	-	< 0.0073
PCB#169(6CL)	0.00090	0.0063	< 0.00070 ~ 0.00128
PCB#189(7CL)	0.0028	0.0017	< 0.0013 ~ 0.0041
Σ_{12} PCBs	0.32	0.14	0.21 ~ 0.47

Table 3. Level of PBDEs of three atmospheric samples in Southern Ocean

	Mean(pg/Nm^3)	SD	Range(pg/Nm^3)
BDE #28(3Br)	0.075	0.018	0.063-0.088
BDE #47(4Br)	0.48	0.086	0.42-0.54
BDE #100(5Br)	0.053	0.0060	0.48-0.57
BDE #99(5Br)	0.14	0.0071	0.13-0.14
BDE #154(6Br)	0.038	0.019	0.020-0.052
BDE #153(6Br)	0.054	0.031	0.023-0.076
BDE #183(7Br)	0.092	0.031	0.054-0.11
BDE #197(8Br)	0.058	0.012	0.049-0.15
BDE #203(8Br)	0.10	0.024	0.085-0.12
BDE #196(8Br)	0.14	0.0057	0.14-0.16
BDE #208(9Br)	0.53	0.066	0.32-0.59
BDE #207(9Br)	0.63	0.073	0.48-0.68
BDE #206(9Br)	1.14	0.0014	0.54-1.1
BDE #209(10Br)	18.09	2.56	9.50-19.90
Σ_{14}PBDEs	21.62	2.70	15.92-23.54